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XIV. *On Salt-Solutions and Attached Water.*

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VIII.

[The paragraphs are numbered in sequence with those of my memoir on *Eutexia*, *antè*, p. 146.]

§ 232. *Introduction.*—When, some ten year sago, the first experiments in this subject were brought before the Physical Society, it was pointed out that the key to the temperature of any salt-ice freezing-mixture was to be found in the temperature of fusion of the cryohydrate of that salt. Since then further light has been thrown upon the subject by the discoveries and observations of others. Thus, Ditté has obtained a hydrate (probably a subcryohydrate) of hydrochloric acid, and Wroblewski has obtained a similar hydrate of carbonic acid. Pettersson, in his exhaustive study of marine ice, made in the ‘Vega’ expedition, has explicitly admitted that the phenomena presented by freezing and frozen sea-water can only be satisfactorily explained by the formation and properties of the cryohydrates. Though this tacit corro-

\* Read May 24, 1884.

boration or explicit adoption by foreigners of the views I ventured to advance has given me perhaps more satisfaction than if they had been only accepted by English physicists, I may be allowed to express some regret that the latter do not yet appear to be awake to the interest and importance of the subject. It gives me, therefore, unusual pleasure to offer them this my eighth memoir on this branch of Molecular Physics.

In this memoir I shall first make a study of the ammonia group in its behaviour with water. I add a little to our knowledge of ammonia itself in this respect. Then are examined the effects of replacing one or more of the hydrogen equivalents by ethyl. Then will be described in some detail the behaviour with water of some aniline salts.

Secondly (§§ 249-255), I shall shift the region of my inquiry upwards on the thermometric scale, and include in it temperatures at which the solid fuses *per se*, and shall thus establish the continuity of the phenomena of fusion with those of solution, making clear the fact that certain bodies, originally solid, may at high temperatures become miscible with water in all proportions. It will be shown how this latter branch of the inquiry, apart from its purely physical interest, has a great geological one, as it throws light on the pyrohydration of igneous formations, just as the cryohydration in flocs has thrown light on the formation of those masses.

§ 233. *Ammonia*.—Anhydrous ammonia,  $\text{NH}_3$ , according to Faraday becomes solid under a pressure of 20 atmospheres at a temperature of  $-75^\circ \text{C}$ . According to Fourcroy and Vauquelin, a perfectly saturated solution (? saturated at air-temperature) freezes between  $-38^\circ$  and  $-41^\circ \text{C}$ ., forming shining flexible needles; at  $-49^\circ \text{C}$ . it freezes to a grey gelatinous mass.

Starting with a 33·3-per-cent. solution, I made solutions of various strengths, and found that pure ice separated from them at the following temperatures:—

TABLE XLV.

Showing Separation of Ice from Solution of Ammonia.

Per cent. of $\text{NH}_3$ .	Per cent. of water.	Temperature of beginning solidification.	Body separated.
1	99	— 0.8	Ice.
3	97	— 3.2	"
5	95	— 5.6	"
10	90	— 12.8	"
15	85	— 21.4	"
20	80	— 43.4	"

Judging by the analogy, which will appear more clear in the sequel, it seems that the body mentioned by Fourcroy is a subcryohydrate, and that the gelatinous mass mentioned still contained too little water for the cryohydrate. I find that a 33.3-per-cent. solution does not crystallize at  $-80^\circ\text{C}.$ ; and I have as yet been unable to obtain the true cryohydrate.

§ 234. *Ethyl-Ammonias*.—The ammonias whose relationship to water have next to be described were obtained from Kahlbaum of Berlin. They were verified by means of their boiling-points, their platinum double chlorides, and by titration with standard hydrochloric acid. Those which I here employ were found to be pure.

§ 235. *Ethylamine*. Boils at  $18^\circ\text{C}.$ —The solutions of this base were made by dropping an indefinite quantity into a narrow-necked weighed bottle, putting in the stopper, weighing, surrounding by a freezing-mixture, and running in the proper quantity of distilled water from a burette. When the quantity of water was small, it was dropped in from a capillary tube until the proper weight was reached.

The first five solutions, namely those containing 0.99, 5, 10, 15, and 20 per cent. of ethyl-ammonia ( $\text{NH}_2\text{C}_2\text{H}_5$ ), showed, on cooling, the separation of the easily recognizable ice-crystals. On further cooling the 20-per-cent. solution, the separating crystals became opaque, betraying the cryohydrate; this occurred at  $-13^\circ.9$ , whereupon the temperature became stationary. After ten or twelve grams had solidified at  $-13^\circ.9$ , the remaining liquid was poured into a fresh tube and reduced to the same temperature. The same operation having been performed three times, the liquid was considered



pure ; 3.589 grams of it were weighed in a stoppered bottle, diluted with water, over-neutralized with hydrochloric acid, evaporated in a water-bath in a platinum dish until the chloride became quite hard on cooling, heated to incipient volatilization, and weighed. There was thus obtained 1.3415 gram chloride of ethyl-ammonium or 0.7407 ethylamine, which corresponds to 20.64 per cent.

On cooling a stronger solution than this, solidification begins at a higher temperature, reaches a maximum between 30 and 35 per cent., and again falls, passing out of the range even of a solid carbonic-acid cryogen. As there is only one tenth of a degree difference between the points of initial solidification of the 30- and 35-per-cent. solutions, and guided by the general shape of the curve, I made a 32.4-per-cent. solution, and found that solidification began at  $-8^{\circ}\text{C}$ .

It is well known that anhydrous ethylamine is not solidifiable in a solid carbonic-acid cryogen. Accordingly, the solid which separates from an aqueous solution of ethylamine of any and every strength between  $-13^{\circ}.9$  and the anhydride is one of those remarkable bodies which I have called subcryohydrates, and which have been observed in the chloride and iodide of sodium.

The subcryohydrate of ethylamine, as a glance at the curve (fig. 1) will show, has a solidifying-point within certainly one tenth of a degree C. of  $-8^{\circ}$ , and, as certainly, it has within two or three tenths of a per cent. the composition of 32.4 per cent. It is minutely crystalline, and of nearly the same specific gravity as the residual liquid. Its solution is eminently supersaturable, and in that state is curiously viscid. It is not easy to see a way whereby it might be made to purify itself in the act of formation. The existence of these solid hydrates of a substance which by itself resists solidification by a carbonic-acid cryogen, and the fact that their melting-points are only ten degrees or so below  $0^{\circ}\text{C}$ ., is surely an unanswerable argument that they are not mere juxtapositions of independent crystals of the two constituents.

Any horizontal line between  $-13^{\circ}.9$  and  $-8^{\circ}$  cuts the curve of aqueous ethylamine in three places. Within these limits, therefore, there are always three degrees of strength of the solution, which begin to solidify at the same temperature.

Thus, if we find an aqueous solution of ethylamine begin to solidify at  $-12^{\circ}$ , we do not know whether it is of the strength 18.7 or 22.2 or 43.3 per cent. Further, it may be noted that, on adding water of the air-temperature to the solid subcryohydrate, a depression of temperature occurs to a point lower than that at which the subcryohydrate stood.

TABLE XLVI.

Separation of Solids from Aqueous Solution of Ethylamine.

Per cent. of Ethylamine.	Per cent. of water.	Temperature at which solidification begins.	Nature of solid.
* 0.9901	99.01	$-0.4$	Ice.
5	95	$-2.0$	"
10	90	$-4.7$	"
15	85	$-8.4$	"
20	80	$-13.3$	"
20.64	79.36	$-13.9$	Cryohydrate.
25	75	$-9.5$	Subcryohydrate.
30	70	$-8.1$	"
32.4	67.6	$-8.0$	"
35	65	$-8.2$	"
40	60	$-10.1$	"
50	50	$-16.4$	"

§ 236. *Diethylamine*.—Let us now replace another equivalent of hydrogen by the same organic radical, and examine the relation towards water of diethylamine,  $\text{NH}(\text{C}_2\text{H}_5)_2$ . This liquid boils at  $54^{\circ}$  ( $57^{\circ}$ , Hofmann) at 31.02 B. The solutions were prepared precisely as in the preceding case.

The four weakest solutions, which contained 5, 10, 15, and 20 per cent. of base respectively, gave no trouble. But from this point the curve (fig. 1) descends very sharply towards the cryohydrate, and rises again with equal steepness. A 22-per-cent. solution yields ice on incipient solidification at  $9^{\circ}.9$ ; while a solution containing only 1 per cent. more, a 23-per-cent. solution, yields subcryohydrate at the same temperature of  $9^{\circ}.9$ . To this difficulty has to be added the circumstance that I have not met with a substance which shows so extraordinary an aptitude for supersaturation. The solutions of the subcryohydrate in the anhydrous base (all those to the right of the cryohydrate in fig. 1) and the cryohydrate itself may be

\* Accidentally taken 1 to 100, instead of 1 to 99.



cooled to  $-20^{\circ}$ , and diligently stirred without showing signs of solidification. The solidification may then be started by a cryogen of solid carbonic acid and ether. Moreover, the solutions near the saturated conditions are as viscid as glycerine; so that the appeal from one part of the liquid to another in the matter of crystallization, and consequent change of composition of the residual liquid, is tardy. These circumstances made it impossible to obtain the cryohydrate pure for analysis in the ordinary way by automatic purification. But they also made it unnecessary; for since a 22 per cent. gives up ice and a 23 per cent. gives up subcryohydrate at the same temperature ( $9^{\circ}9$ ), it follows that a 22.5-per-cent solution must, within a probable error of about 0.2 per cent., have the composition of the cryohydrate. Having made such a solution, and cooled it to  $-10^{\circ}$  in a salt-ice cryogen, the bottom of the tube containing it was dipped in a little carbonic-acid cryogen until a little white opaque regulus of crystals was formed. The whole being then restored to the ice-salt cryogen and stirred, opaque solidification began, the rounded tufts of crystals much resembling oatmeal in suspension. From first to last the temperature now remained constant at  $11^{\circ}0$  C. Of course there was no need to analyze a body thus synthesized.

TABLE XLVII.

Separation of Solids from Aqueous Solution of Diethylamine.

Per cent. of Diethylamine.	Per cent. of water.	Temperature of initial solidification.	Nature of solid.
5	95	$-1^{\circ}1$	Ice.
10	90	2.9	"
15	85	5.2	"
20	80	8.4	"
21	79	9.1	"
22	78	9.9	"
22.5 ( $\pm 0.2$ )	77.5 ( $\mp 0.2$ )	11.0	"
23	77	9.9	Cryohydrate.
25	75	9.1	Subcryohydrate.
30	70	8.3	"
35	65	8.0	"
40	60	8.2	" (pure)
45	55	8.6	"
50	50	9.1	"
60	40	12.2	"
70	30	23.4	"

Diethylamine does not solidify in a carbonic-acid cryogen.

§ 237. *Triethylamine*,  $N(C_2H_5)_3$ . Boils at  $88^\circ$ .—Viewed as an anhydride, we should expect, *à priori*, to find a greater difference between the physical properties of this body and those of diethylamine than between those of the latter body and ethylamine. Indeed, the difference might be expected to be comparable with that existing between the properties of ethylamine and those of ammonia; for the replacement of the first and the last equivalent of hydrogen by ethyl would be expected to effect a difference of kind, while the replacement of two instead of one would effect rather an alteration in degree. Be this as it may, the properties of triethylamine in reference to water are quite exceptional, or at least very remarkable. The solutions of strengths 5, 10, and 15 per cent. yielded ice; the latter and the 20 per cent. can be employed for obtaining the cryohydrate, but the 20 per cent. begins its solidification with the subcryohydrate. The solidifying temperature of the cryohydrate is  $-3^\circ.8\text{ C}$ . This cryohydrate contains 19.15 of the anhydrous base. It may be remarked that the hydrochloride of this base retains hydrochloric acid with such firmness that, even when heated to incipient volatilization, it still remains acid\*.

The subcryohydrate of this body is, like those of the previously examined ones, very prone to supersaturation; so that, in examining the richer solutions, it is advisable to have recourse to the solids of previous preparations; which act like a ferment. A nearly remelted tubeful of the subcryohydrate, set to resolidify very slowly, crystallizes in bright laminæ one or two millimetres in diameter. More quickly frozen in repose, crystalline masses an inch long are fashioned upon the glass.

\* A few grains of chloride of triethyl-ammonium heated on a hot spatula exhibit a beautiful phenomenon. The columns and whirls of white smoke can be watched petrifying in the air to white soot without much change of form.

TABLE XLVIII.

Separation of Solids from Aqueous Solutions of Triethylamine.

Per cent. of Triethylamine.	Per cent. of water.	Temperature of initial solidification.	Nature of body formed.
5	95	— 1.0	Ice.
10	90	— 2.0	"
15	85	— 2.9	"
18	82	— 3.4	"
19.1	80.9	— 3.8	Cryohydrate.
20	80	— 3.5	Subcryohydrate.
30	70	— 4.1	"
40	60	— 5.1	"
50	50	— 6.7	"
70	30	— 13.6	"
80	20	— 20.6	"

For the curve, see fig. 1, p. 179.

§ 238. Triethylamine is one of those rare bodies which, like sulphate of sodium, sulphate of calcium, caustic lime, and a few others, are more soluble in cold than in hot water. The behaviour of the three bodies named is clearly traceable to the decomposition by heat of definite hydrates. Without laying undue stress upon this, it seems that the phenomenon in question is one of decomposition, which so often follows increased temperature, and not an inversion of the rule that solubility also increases with temperature. The body decomposed in the case before us is clearly a hydrate—either the cryo- or subcryohydrate. Accordingly, though striking in its presentation, the phenomenon is really quite continuous with the decomposition by heat of oil of vitriol; which decomposition, I presume, does actually take place when that liquid is heated above its boiling-point (in a closed vessel). But while in the latter case the products of decomposition are probably miscible, and mix, though held apart from chemical union by heat-tension, with the hydrates of ethylamine the products of thermal decomposition are separated not only chemically but in mass, because, when chemically separated, they are not molecularly miscible, at least in all proportions.

The following table shows the temperatures at which turbidity begins and ceases in aqueous solutions of triethylamine of various strengths. (See also fig. 1, "Triethylamine and Water as liquids.")



TABLE XLIX.

Separation in Aqueous Solutions of Triethylamine.

Per cent. of Triethylamine.	Per cent. of water.	Critical temperature between clearness and turbidity.	Remarks.
1.96	98.04	78°	{ Becomes clouded, and begins to boil.
3.85	96.15	41	
5	95	34	
8	92	23.5	
10	90	21.3	
15	85	18.8	
18	82	18.6	
20	80	18.6	
30	70	18.2	
40	60	18.4	
46.46	53.54	18.3	
50	50	18.4	
70	30	17.1	
80	20	13.4	
90	10	6.1	
94.5	5.5	-7 (about)	{ Complete liquid solubility at all temperatures.
99	1	.....	

A solution containing only 0.99 per cent., sealed in a very strong glass tube and heated to 200° C., did not show any opalescence.

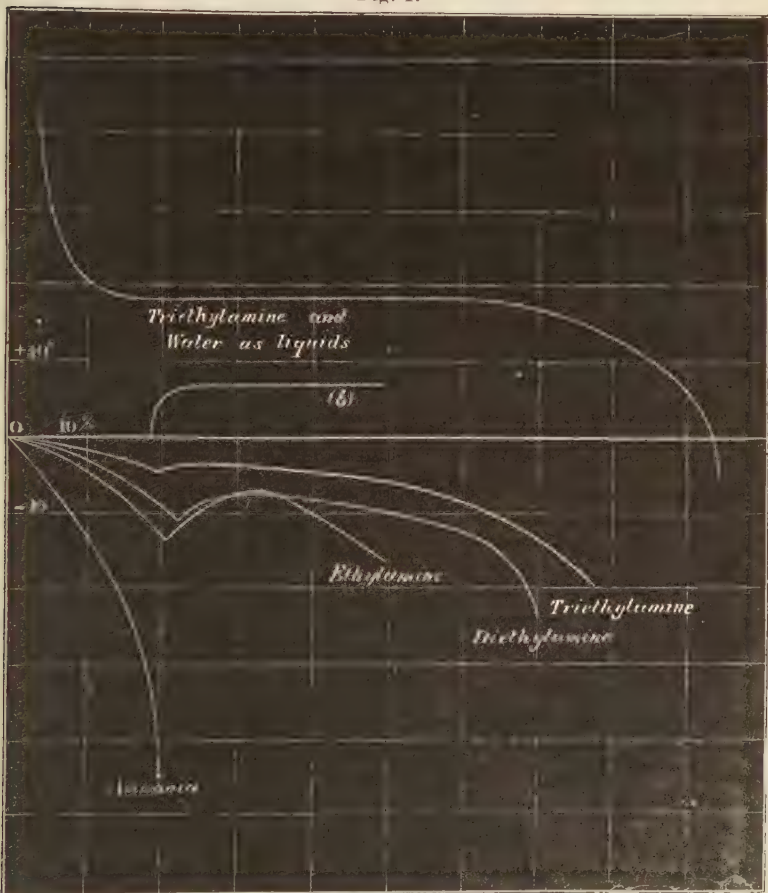
A 1.96-per-cent. solution begins to give off bubbles of gas at the same temperature at which it becomes turbid. A still more dilute solution, namely a 0.99 per cent., does not become turbid at 200° C., when it is heated in a sealed tube. The curve (fig. 1, "Triethylamine and Water as liquids") shows the relationship above examined. The following example illustrates the history of a solution. Ten grams of ethylamine and 90 grams of water, shaken together at 25°, form a white emulsion. On standing at that temperature, two transparent layers are formed, of which the upper is ethylamine saturated at 25° with water, and the lower water saturated at 25° with ethylamine. On heating to 28°, both layers become turbid; the upper sheds water saturated at 28° with ethylamine, which falls, and the lower ethylamine saturated at 28° with water, which rises. These new quantities join their respective camps, the constitution of which has, of course, been altered by the departures, and is now that of saturation at the new tempe-

perature in the two cases. The surface of demarcation shifts towards the centre of the mass. Similar effects follow further rises of temperature. Let now the tube cool. The former condition is reestablished. On further cooling, the surface of demarcation shifts—rises in this case as the two liquids mix more with one another. At  $21^{\circ}3$  perfect solution ensues, and this is well marked within a tenth of a degree. Just above this temperature the mass is opalescent, just beneath it it is perfectly limpid. When at this critical temperature, the warmth of the hand only momentarily applied makes a wide test-tube of the limpid mixture quite milky. Nor can such a test-tube be passed so nimbly through a flame as not to exhibit the same change. Following the temperature downwards, we find the solution remains clear below  $0^{\circ}$ , until we reach  $-2^{\circ}$ , whereupon crystals of ice appear. These increase with the falling temperature until  $-3^{\circ}8$  temperature and 10.1 per cent. is reached. The cryohydrate now solidifies, and no further percentage change is possible; nor temperature change, until solidification is complete.

A 40-per-cent. ratio only shows perfect mixture at  $18^{\circ}4$ . It remains a mixture until  $-5^{\circ}1$ , whereupon subcryohydrate begins to appear in the solid form. Its quantity goes on increasing with lowering temperature until  $-20^{\circ}6$  is reached: this marks an 80-per-cent. solution. At still lower temperatures no doubt the liquid becomes more enriched. If the anhydrous liquid is unsolidifiable by cold, then the ordinate at 100 per cent. is asymptotic; but if, as is more likely, the liquid is solidifiable, the remainder of the water and of the ethylamine will unite to form some hydrate even lower than the subcryohydrate at some very low but constant temperature. An 80-per-cent. ratio at  $-30^{\circ}$  is thick with solid subcryohydrate. Perfect liquefaction takes place at  $-20^{\circ}6$ . The liquid remains clear until  $+12^{\circ}$  is reached. At and above  $12^{\circ}$  separation ensues, which increases with the increasing temperature. The curve (fig. 1, "Triethylamine and Water as liquids") is virtually a straight line between 15 per cent. and 50 per cent. The deviations are probably errors of observation; and these errors of observation are certainly not due to want of definition of the occurring and vanishing turbidity, which is well marked within 0.025 of a degree. Nor are they

due to errors of original weighing or change during manipulation; for the very flatness of the curve shows that a great change of composition has little effect upon the temperature of saturation. If they are indeed errors, they arise probably from the collecting together of the opalescing globules into clear drops which separate down, leaving the liquid above as clear as though it had been cleared by cold. The indication

Fig. 1.



from a gradually ascending temperature is accordingly more to be relied on than one from a falling temperature.

When water is added to triethylamine, but little heat is



evolved. A very small rise in temperature occurs when the 30-per-cent. mixture is made. The constituents should be brought to about  $10^{\circ}$ ; and in the final experiment the thermometer and thin glass bulb, in which the mixture is effected, are to be previously warmed fully to the temperature at which they stood at the end of the previous experiment. It is probable that the smallness of the heat of combination is nearly connected with the ease of thermal separation. It is to be noticed, moreover, that in the region of the lower curve about the suberyohydrate, where the curve is flat because great change of *percentage* makes little difference in temperature of initial solidification, the curvature of the upper curve, fig. 1, "Triethylamine and Water as liquids," is also nearly nothing. Whether above or below zero, we are dealing apparently at every individual percentage with the same substance, the suberyohydrate: it is this region which is so keenly sensitive to changes of temperature.

§ 239. There is this important and essential difference between the genesis of a cryohydrate and that of a suberyohydrate. Solutions of nearly the cryohydrate strength approach the composition of that body as they lose heat and sink in temperature—weaker ones by the shedding of water (as ice), stronger ones by the shedding of salt or suberyohydrate. And this is true for all solutions from 0 per cent. up to the strength of the suberyohydrate; that is, on the curve, to the point where  $\frac{dx}{dy}$  changes sign.

Not so with the suberyohydrate. A solution weaker than the suberyohydrate, to the left of it on the figure, will "run down" to the cryohydrate by dint of shedding the suberyohydrate. A solution stronger than the suberyohydrate will "run down" to the solidifying-point of the anhydrous liquid or to that of some secondary cryohydrate, no example of which is, I think, yet known. In either case, the liquid residue gets further and further away from the ratio in the suberyohydrate. The whole condition may be illustrated by the motion of a marble rolling upon the curve. It will run down to the bottom of the valley of the cryohydrate wherever it is placed on the slopes of that valley, and there remain in stable equilibrium. But placed upon the top of the great swell of

the subcryohydrate, it will be at rest only if undisturbed, and so be in instable equilibrium. It will, if disturbed, either roll down to the bottom of the cryohydrate valley, or roll into the abyss of the anhydrous liquid. The cryohydrate is the level of a lake. The subcryohydrate is the watershed (subcryohydrate shed) of a hill-range.

The cryohydrate being an eutectic alloy, the subcryohydrate is a definite chemical combination, existing probably as such in the liquid when above zero, and liberating in its formation the heat observed when the two liquids are mixed; and as, for instance, sulphate of soda crystallizing either from an acid or alkaline solution leaves the liquid more acid or more alkaline than before, so the subcryohydrate in its solidification leaves the liquid from which it separates continuously more aqueous or less aqueous according as it started from a solution more or less aqueous than itself. The "more" and "less," as here employed, refer of course to intensity, not to quantity, and the change is the analogue of that suffered by electricity when the surface of a conductor alters in size.

§ 240. *Some Applications of the above Property of Triethylamine.*—It appears from Table XLIX. that one weight of triethylamine with 19 weights of water is a ratio requiring  $34^{\circ}$  C., or  $93^{\circ}5$  F., that is a low blood-heat, to effect its turbidity. A ratio of 1 of ethylamine and 24.76 of water requires  $41^{\circ}$  C. or  $105^{\circ}8$  F. for the same effect to be produced: this is a fever heat. Accordingly, a few little glass capsules containing solutions of the triethylamine of strengths graduated between these two and thereabouts, and containing also a little mercury to assist the stirring-up when shaken, may be of use in the diagnosis of fever. The eye may be fastened to a thread or rod, and so introduced beneath the arm or into the cavities. I have made a series of 9 such capsules, which show turbidity at F.



68 $^{\circ}$ 3, 69 $^{\circ}$ 4, 76 $^{\circ}$ 1, 79 $^{\circ}$ 9, 91 $^{\circ}$ 4, 98 $^{\circ}$ 6, 105 $^{\circ}$ 2, 111 $^{\circ}$ 2, 123 $^{\circ}$ 8.

§ 241. The radiation from an electric arc passing into an 8-per-cent. solution will warm it to opacity. Thin strips of variously coloured glass placed in such solutions will determine the opalescence after various time lapses,—the red glass acting the slowest, and the others, speaking broadly,

the quicker the shorter the wave-length of the light they transmit. Two of complementary colour, which together absorb all radiation, or a single black one, act the quickest. Coloured glasses placed between the solution and the source of radiation cause opalescence in times which are the longer the shorter are the transmitted wave-lengths.

A few drops of the solution placed as a thin film between two thin sheets of flat glass, and prevented from evaporation by sulphur-cement around the edges, forms a sensitive plate. The hand placed upon it leaves a white silhouette. The spectrum thrown upon this plate leaves a transient record.

It is probable that the heat liberated when triethylamine is mixed with water is, if the expression may be allowed, the real image of the heat which on entering the mixture effects separation. They are both equal in quantity to the heat of suberyohydration; the former being that heat itself. It is a happy circumstance that the temperature at which separation begins within the limits of 20 to 50 per cent. solutions is a usual atmospheric temperature, namely  $18^{\circ}3$  C. ( $64^{\circ}94$  F.).

§ 241 *a*. The quantitative relationship in respect to solubility existing between water and triethylamine was determined with considerable accuracy in the following manner. A 50 c. c. burette graduated to two-tenths was sealed at one end, and the mercury and water-meniscus values determined. It was drawn out to a narrow neck, and received about 2 c. c. of mercury. The whole being now counterpoised, a few c. c. of ethylamine were introduced, which proved to weigh 6.86 grams. A few grams of water were next added, the end sealed off and dried, and the whole reweighed. It was found that 7.885 grams of water were present.

The whole was now brought to a temperature low enough to ensure perfect mixture, and then gradually heated in a large beaker of water to which successive portions of warmer water were added. The water was diligently stirred. When the temperature is high enough to cause separation, the tube is kept at that constant temperature for half an hour, being repeatedly shaken. Taking the level of the mercury as constant, and calling it, when corrected for meniscus, 0, we have first the height of the plane of separation of the two liquids to read off. This requires no correction for meniscus at temperatures below  $25^{\circ}$  C. At  $30^{\circ}$  and  $50^{\circ}$  there is some + cur-



vature (like water); this I have neglected. The height of the upper surface has to be read and corrected for meniscus. (For this the same correction is taken as for water.) The volume of water at  $15^{\circ}$  was 7.88 c. c., and the volume of triethylamine was 9.5 c. c. On bringing the two together, sufficient heat was set free by the mixture of part to prevent the mixture of the whole. On cooling to  $15^{\circ}$  the two mixed perfectly, and the volume was 16.6, showing therefore a contraction of 0.8 c. c. At  $18^{\circ}3$  the liquid still remained clear, but at  $18^{\circ}7$ , that is in half a degree, a great separation had occurred. In the following table the corrected readings are given.

Separation between water and triethylamine (Triethylamine 46.45 per cent., Water 53.55 per cent.).

At	Vol. of lower stratum.	Vol. of upper stratum.
$15^{\circ}0$ . . . .	0	16.6
$18^{\circ}3$ . . . .	0	16.6
$18^{\circ}7$ . . . .	3.5	13.2
$19^{\circ}0$ . . . .	4.5	12.2
$20^{\circ}0$ . . . .	6.1	11.4
$21^{\circ}0$ . . . .	6.8	10.1
$22^{\circ}0$ . . . .	7.2	9.7
$25^{\circ}0$ . . . .	7.8	9.3
$30^{\circ}0$ . . . .	7.9	9.4
$50^{\circ}0$ . . . .	8.0	9.7

So nearly complete is the separation at  $25^{\circ}$ , that above this temperature the upper stratum gives more in volume by expansion by heat than it loses by the rise of the plane of demarcation. To get an idea of the completeness of the separation at  $50^{\circ}$  C., we may compare the volume of the lower stratum at  $50^{\circ}$ , which is 8.0, with that of 7.885 grams of water at  $50^{\circ}$ , which is 7.93. This signifies that at  $50^{\circ}$  the lower stratum must be nearly pure water, and the upper nearly pure ethylamine. For the plane of separation stands only  $\frac{1}{80}$  of the height of the original water-column above that height. See fig. 1, curve *b*.

§ 242. *Thermal Relation of some Aniline Salts to Water.*---

In turning to organic ammonias and their salts which contain radicals of greater molecular weight, and belonging to different series from those we have been considering above, we are tempted by aniline. It can be got in a state of great purity. Its salts are well defined and stable, and of various degrees of

solubility. The aniline I employed was rectified several times, converted into the chloride, and twice recrystallized; reconverted into the base by caustic potash, dried, and finally distilled.

Aniline is slightly soluble in water. On cooling to a temperature of  $-0^{\circ}7$ , the water and aniline solidify together as a porcelain-like opaque cryohydrate, which is, however, too poor in aniline to be capable of satisfactory analysis.

§ 243. *Chloride of Aniline*.—As a cryogen, the chloride of aniline gave a temperature of  $-10^{\circ}5$ . For its solubility the weighed solution was evaporated in a water-bath until it ceased to lose weight. Saturated at  $13^{\circ}1$ , it was found that 8.3210 grams gave 3.8875 anhydrous salt, or 46.72 per cent. Saturated at  $0^{\circ}$ , 13.2836 grams gave 5.3595 grams dry salt, or 40.35 per cent. The solution saturated at  $0^{\circ}$ , or a 20-per-cent. solution placed in a freezing-mixture, falls to the temperature of  $-10^{\circ}7$ . It is here as generally preferable to reach the cryohydrate from the dilute side. This cryohydrate readily forms a supersaturated solution. Of the cryohydrate, 7.1760 grams gave 2.2860 dry salt, or 31.86 per cent.

Percentage solutions were then made, and their temperatures of initial solidification determined.

TABLE L.

Chloride of aniline per cent. by weight.	Water per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
1	99	$-0.2^{\circ}\text{C.}$	Ice.
4	96	$-1.0$	"
5	95	$-1.3$	"
6	94	$-1.6$	"
7	93	$-1.9$	"
8	92	$-2.2$	"
9	91	$-2.5$	"
10	90	$-2.8$	"
11	89	$-3.0$	"
12	88	$-3.3$	"
13	87	$-3.6$	"
20	80	$-5.7$	"
25	75	$-7.2$	"
30	70	$-9.0$	"
31.86	68.14	$-10.7$	Cryohydrate.
35	65	$-8.0$	Salt.
40.35	59.65	0	"
46.72	53.28	$+13.1$	"

The curve corresponding to the above table is shown in fig. 2.

§ 244. *Nitrate of Aniline*.—As a cryogen, the temperature  $-2^{\circ}2$  was obtained. A solution saturated at  $13^{\circ}1$  was evaporated *in vacuo* over sulphuric acid until it ceased to lose weight; 7.5174 grams gave 1.1710 gram dry salt, or 15.58 per cent. 8.6860 grams of solution saturated at  $0^{\circ}$  gave 0.9500 gram, or 10.94 per cent. A dilute solution reached, in a freezing-mixture, the constant temperature of  $-2^{\circ}2$ . Of this, the cryohydrate, 7.7972 grams gave 0.8270 gram dry salt, or 10.61 per cent. The nitrate cannot be dried in a water-bath without suffering partial decomposition. The above results are embodied in the following table, which also shows the temperatures of initial solidification.

TABLE LI.

Nitrate of aniline per cent. by weight.	Water per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
2	98	$-0.4$	Ice.
4	96	$-0.8$	"
6	94	$-1.1$	"
8	92	$-1.5$	"
10	90	$-2$	"
10.61	89.39	$-2.2$	Cryohydrate.
10.94	89.06	0	Salt.
15.58	84.42	$+13.1$	"

Fig. 2 shows the curve representing the above numbers.

§ 245. *Sulphate of Aniline*.—This salt was recrystallized three times, and after drying between blotting-paper was finally dried before a brisk open fire. As a cryogen it showed a temperature of  $-0^{\circ}8$ . Of the solution saturated at  $13^{\circ}1$ , it was found that 25.6925 grams gave 1.5000 dry residue, or 5.84 per cent. Of the solution saturated at  $0^{\circ}\text{C.}$ , 8.8675 grams gave 0.4357 gram, or 4.91 per cent. The solidifying temperature of the cryohydrate was found to be  $-0^{\circ}9$ , and 9.5607 grams of it gave 0.4620 gram dry salt, or 4.83 per cent. This salt appears to melt in its water of crystallization, and takes a long time to dry. The following table contains the above results, together with the temperature of initial solidification



in solutions of several strengths. The sparing solubility of the salt limits the table very much.

TABLE LII.

Sulphate of aniline per cent. by weight.	Water per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
1	99	- 0.1	Ice.
2	98	- 0.2	"
4.5	95.5	- 0.6	"
4.83	95.17	- 0.9	Cryohydrate.
4.91	95.09	0	Salt.
5.84	94.16	+13.1	"
15.35	84.65	100.0	"

The curve representing this table is found in fig. 2.

§ 246. *Oxalate of Aniline*.—8.3230 grams of the oxalate of aniline saturated at 14°5 gave 0.1080 gram dry salt, or 1.29 per cent. At 0° I obtained 0.0320 gram of the dry salt from 10.8170 grams solution, which means only 0.29 per cent. The cryohydrate was formed at the very high temperature of -0°4. On evaporation, 8.5450 grams gave 0.02 gram dry salt, or only 0.14 per cent. The sparing solubility of the salt in water prevented me from examining solutions of strengths weaker than the cryohydrate.

TABLE LIII.

Oxalate of aniline per cent. by weight.	Water per cent. by weight.	Temperature at which solidification begins.	Nature of solid.
0.14	99.86	- 0.4	Cryohydrate.
0.29	99.71	0	Salt.
1.29	98.71	+14.5	"

For curve see fig. 2. Although the temperature here shown for the cryohydrate is distinctly below zero, proving that the oxalate is not, like a colloid, molecularly free from the water, yet I am not assured that I have been able to form a true cryohydrate in the solid form. The ice and salt separate apart, the former adhering to the glass, and the microscopic

transparent crystals of the latter remaining in suspension in the solution. The first analysis, indeed, showed greater percentage of salt at  $-0^{\circ}4$  than at  $0^{\circ}$ , the difference amounting to about 0.28 per cent. on the highest. This is an impossible result. The state of things clearly arose from the circumstance that the liquid cryohydrate was enriched by the suspended crystals. The solution at  $0^{\circ}$  was also abnormally rich from the same cause. It was only on keeping the solution in ice for twenty-four hours that the zero amount above given was obtained, and by keeping the zero solution for twelve hours in a weak freezing-mixture (nitre and ice) that the cryohydrate (in a liquid form) was got.

§ 247. *Salicylate of Aniline*\*.—The above remarks are again applicable to this salt. So sparingly is it soluble in water at all temperatures, and so close below  $0^{\circ}$  is the cryohydrate, that no examination of this region was practicable. Of a solution at  $0^{\circ}$ , 10.3720 grams gave 0.0295 gram, or 0.28 per cent. The cryohydrate formed at  $-0^{\circ}05$  or  $-0^{\circ}07$ . Of it, 10.0310 grams gave 0.0245 gram, or 0.24 per cent. A solution saturated at  $6^{\circ}2$  gave 0.0710 gram salt out of 10.9270 grams solution, that is 0.65 per cent. Even at  $16^{\circ}8$  there was only obtained 0.0800 gram from 10.3450 grams, or 0.77 per cent.

TABLE LIV.

Per cent. of salicylate of aniline by weight.	Per cent. of water by weight.	Temperature at which solidification begins.	Nature of solid.
0.24	99.76	$-0^{\circ}06$	Cryohydrate.
0.28	99.22	0	Salt.
0.65	99.35	+ 6.2	"
0.77	99.63	+ 16.8	"

For the graphic representation of these numbers see fig. 2

\* The salicylate of aniline has not, I believe, been previously described. It is obtained by mixing an alcoholic solution of aniline with the acid. It fuses at about  $150^{\circ}$ , and cannot be distilled without decomposition. It is slightly soluble in bisulphide of carbon; soluble in ether, hot or cold; soluble in alcohol, hot or cold; soluble in hot benzol, very sparingly in cold.

§ 248. *Pyrogallate of Aniline*\*.—3.7270 grams of the solution saturated at  $17^{\circ}8$  yielded 1.7440 gram dry salt *in vacuo*, or 46.80 per cent. Of a solution saturated at  $0^{\circ}$  C., 5.92 grams gave 1.992 gram of the dry salt, or 33.65 per cent. As a cryogen the temperature  $-4^{\circ}6$  was obtained, and the cryohydrate showed the same temperature. 9.397 grams of cryohydrate gave 2.253 of salt, or 23.98 per cent. The above results, and the separation of solid matter on loss of heat, are exhibited in the following table:—

TABLE LV.

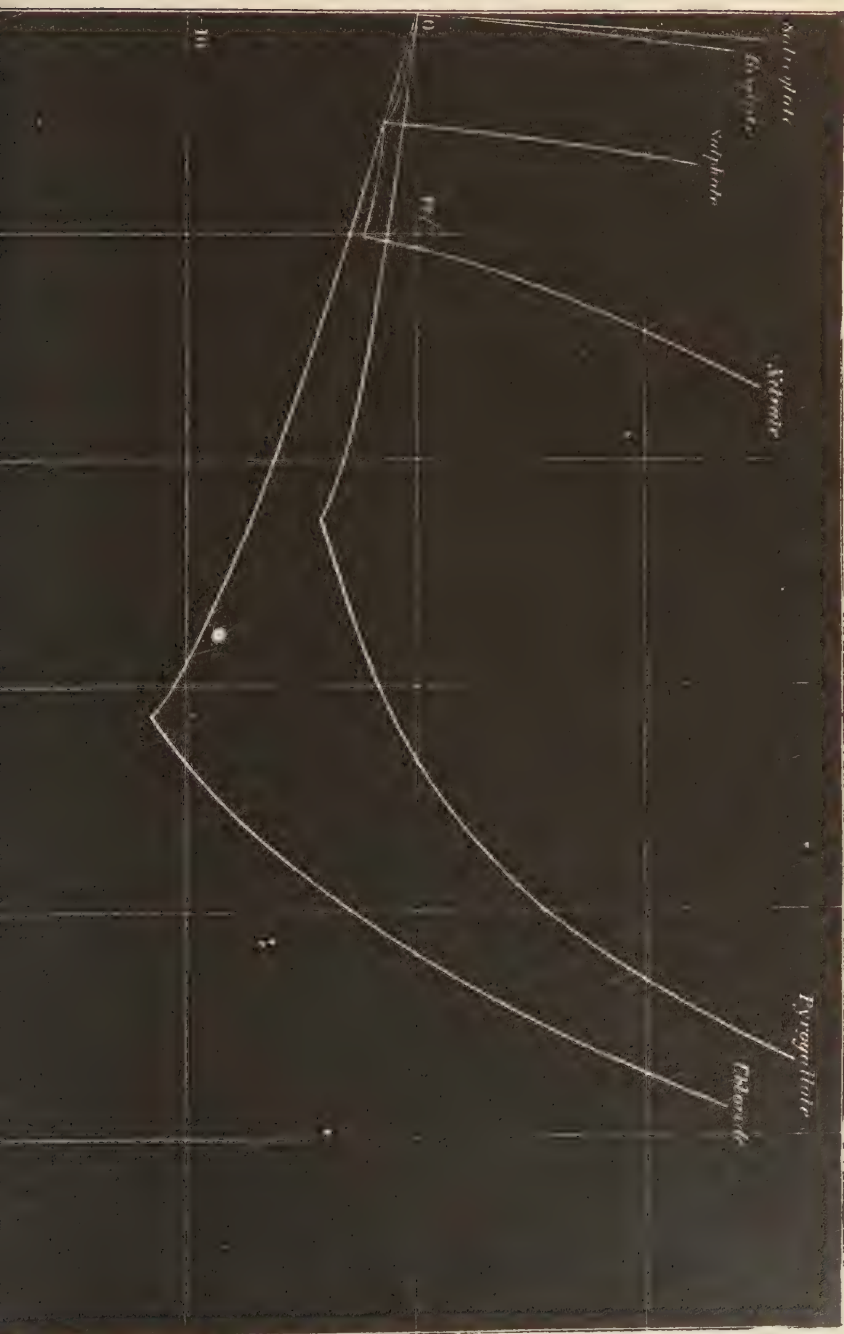
Per cent. of pyrogallate of aniline by weight.	Per cent. of water by weight.	Temperature at which solidification begins.	Nature of solid.
9.09	90.91	$- 1^{\circ}0$	Ice.
20.00	80.00	$- 2^{\circ}7$	"
23.98	76.02	$- 4^{\circ}6$	Cryohydrate.
33.65	66.35	0	Salt.
46.00	54.00	$+ 17^{\circ}8$	"

The curve corresponding to these numbers is found in fig. 2. It is to be noted that amongst all the curves referring to the aniline salts, that belonging to the nitrate alone has a well-marked concavity on its ascending branch (from the cryohydrate to the right) turned towards the axis of strength. The very important signification of this curvature will form the key to much in the next Chapter referring to the limit of solubility, or rather to the unlimited solubility in certain cases of certain salts, especially nitrates.

\* As I do not find any account of this body, I may briefly note its preparation and properties. On mixing the two substances pyrogallie acid and aniline, a dry hard mass is obtained. As this is soluble in aniline, only a slight excess of the latter is used. The solid mass is dissolved in a minimum of hot benzol; cooled to about  $5^{\circ}$ , filtered, and washed with cold benzol. Amongst its properties are the following:—It fuses at  $126^{\circ}$  C. or  $128^{\circ}$  C. It is very soluble in water, hot and cold; also in hot and cold alcohol and ether; soluble in hot benzol, very sparingly in cold; very sparingly soluble in bisulphide of carbon, hot or cold. Fused on glass, it forms a beautiful crystalline film, the crystals being several inches long. It is anhydrous. In another preparation, 1 part of pyrogallie acid was dissolved in 4 parts of water at  $50^{\circ}$ . Aniline was added until a specimen became cloudy on cooling. It was cooled to about  $10^{\circ}$  and filtered through wet paper. It was then evaporated to about half its bulk and dried *in vacuo* over sulphuric acid. It turns brown on exposure to the air.



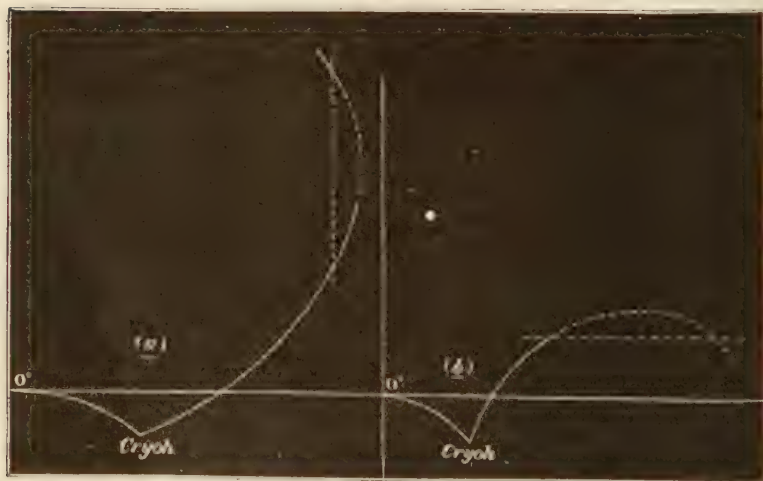
Fig. 2.—Aniline Salts.



*Infinite Solubility.*

§ 249. An examination of curves of solubility of salts in water, drawn so that the ordinates are temperatures and the abscissæ are percentages, reveals two types of curves, which differ only essentially in their right-hand or salt-saturated branches. Iodide and bromide and, perhaps, chloride of sodium may be taken as the type of *a*, fig. 3, and nitre of *b*, fig. 3 (see § 126). The curvature of the right-hand branches of both curves must diminish as we travel from the cryohydrate in the direction of the arrows, otherwise there would be two temperatures at which there is the same solubility (*a*, fig. 3, dotted lines) for every solubility between certain limits; or (*b*, fig. 3, dotted lines) there would be two solubilities for every temperature between certain limits. If we concede the

Fig. 3.



impossibility of these conditions, there appear to be three alternatives—the curve loses curvature either parabolically or hyperbolically, or there must be contrariflexure. The first would carry the conditions into the region of critical state and decomposition. The second might mean, in the case of *a* type, if such asymptote be also parallel to the ordinates, that a certain per cent ratio of salt is soluble in water at a certain temperature, and at all higher temperatures; in the case of *b*

type, if such asymptote be parallel to the abscissæ, that at a certain temperature a finite mass of water will dissolve an infinite mass of salt.

For the experimental examination of this curious question the salt-alloy of nitrate of lead and nitrate of potash, described in § 215, is excellently well adapted. Its composition is 46·86 nitrate of lead + 53·14 nitrate of potash, and its fusing-point, being 207°, is well within the range of the mercurial thermometer. Its constituents at this temperature are far below their temperature of decomposition, and, what is of equal importance, both the nitrates are essentially anhydrous at all temperatures above 0° C.

§ 250. *a* grams of this salt-alloy, finely powdered and freed from condensed moisture, were introduced into a weighed tube. A little water being then introduced through a capillary tube, the end was sealed off, and both reweighed, the amount of water introduced being thus known. The sealed tube was wrapped round in two places with copper wire, and placed in a copper oil-bath. The bath was heated till complete fusion was effected, the water and salt completely mixing to a colourless limpid liquid. The wire enables the tube to be taken out and the contents moved to and fro.

When complete fusion is obtained the bath is allowed to cool slowly, being kept well stirred. The temperature of incipient solidification is observed several times, to avoid possible errors arising from supersaturation, although with this salt-alloy no such condition appears to obtain. As considerable pressure may be exerted on the tube, it and the thermometer were viewed through two sheets of glass six inches apart. None of the tubes, however have burst.

The following results were obtained:—

Percentage of Salt.	Solidifying temperature.
100	207°
99·82	203° or 204°
98·24	197°

§ 251. These results are striking and important. The phenomenon of fusion *per se* is continuous with, and nothing more than an extreme case of, liquefaction by solution. When



we are considering such a case as the second, near the top, where 0.18 weight of water dissolves 99.82 of salt, we are induced to regard it as a solution of water in the fused salt rather than the converse, especially as the solidifying-point is so near that of the dry salt. It will be readily granted that a proportion of the alloy and water having even less water than the above will have an incipient solidifying temperature even closer to the temperature of fusion of the dry alloy. Hence the question, Is this a case of fusion or solution? is to be answered by the reply, It is continuous with both.

The above results with this salt-alloy gave encouragement for the examination of nitre alone with water. The thermal relationship of nitre and water from  $-3^{\circ}$  C., the melting-point of the cryohydrate, to the boiling-point of a saturated solution at one atmospheric pressure, about  $115^{\circ}$  C., has been pretty fully examined by others and myself. The results are shown in Table LVI. The first sixteen are from my memoir IV., § 129; the next five are on the authority of Gay-Lussac; the last seven, which are those to which I wish here to direct particular attention, are obtained by the use of sealed tubes as described in § 240. The result corresponding to  $T = 115^{\circ}$  is interpolated for the sake of verification from Table LVII. § 253, where a different method of experimenting was undertaken for a different purpose. For  $T = 100^{\circ}$  C., the solution saturated at  $114^{\circ}$  C. was allowed to cool for several hours in a tube surrounded by boiling water (16.05 grams gave 11.485 grams nitre). For  $T = 109^{\circ}$  C., the solution saturated at  $114^{\circ}$  C. was allowed to cool for several hours in a tube surrounded by a boiling saturated solution of chloride of sodium (17.83 grams of the solution gave 13.2945 grams of nitre).

§ 252. It must not be overlooked that, although the tubes in the last seven experiments were filled as full of the nitre as the exigencies of manipulation permitted, a certain air-space was unavoidably left into which the water in the tube was free to evaporate. In the last one, indeed, in which water was present its actual weight was only 0.114 gram. This, heated by itself in the free space to  $300^{\circ}$  C., would have become dry superheated steam. But the fact that it lowered the temperature of solidification  $20^{\circ}$  C. shows that in the presence of nitre it is not all

free. The vapour-tensions of strong solutions of nitre will have to be determined. Correlation with this table or with Wüllner's results is all the more necessary, because, as has been shown by Sorby and others, variation in pressure is not without influence on solubility as well as upon fusion, *per se*.

TABLE LVI.

I.	II.	III.	
A solution of nitre in water containing the following percentage of nitre,	that is, to 1 weight of water containing the following weights of nitre,	begins to solidify at the following temperature C.,	giving up as a solid the following:—
0	0.0000	0.0	Ice.
1	0.0101	-0.1	"
2	0.0203	-0.3	"
3	0.0309	-0.7	"
4	0.0417	-1.1	"
5	0.0526	-1.5	"
7	0.0753	-2.2	"
8.5	0.0929	-2.6	"
10	0.1111	-2.9	"
11.2	0.1261	-3.0	"
12	0.1364	0.0	Cryohydrate.
13	0.1481	+2.0	Nitre.
15	0.1765	+6.0	"
20	0.2500	+14.0	"
25	0.3333	+21.0	"
35	0.5385	+35.0	"
40	0.6667	+41.0	"
*43.3	0.7637	+45.1	"
*49.2	0.9685	+54.7	"
*55.4	1.2421	+65.4	"
*62.5	1.6667	+79.7	"
*70.3	2.3663	+97.6	"
71.56	2.5162	+100.0	"
74.56	2.9308	+109.0	"
74.97	2.9956	+114.0	"
75.2	3.0323	+115.0	"
79.14	3.7939	+123.0	"
84.67	5.5231	+151.0	"
89.94	8.9404	+201.0	"
95.11	19.4499	+262.0	"
98.86	86.7193	+300.0	"
100.00	∞	+320.0	"

\* Gay-Lussac.

The graphic representation of this relationship is shown in fig. 4, curve A, an ordinate of 1° C. being taken equal to an abscissa of 1 per cent. of nitre. The curve, after dipping to the

Fig. 4.





cryohydrate, rises through  $0^{\circ}$  C. and reaches the 100 per cent. at  $320^{\circ}$  C. Perhaps curve B shows the relationship better. It is traced from columns II. and III. It is asymptotic to the temperature-line  $320^{\circ}$  C., and shows how fused nitre and fused ice are miscible with one another in all proportions.

§ 253. *Boiling-Points of Solutions of Nitre.*—To determine the boiling-points of solutions of nitre of various strengths, 40 grams, which were in the later experiments made up to 100 grams, were placed in a clean tin vessel having a narrow neck, together with a thermometer and an indefinite amount of water. The whole was supported in a hot-air chamber so that the neck only of the tin vessel projected. An arrangement was also made for blowing hot air through the upper part of the vessel. By this arrangement it was hoped that the amount of water condensed in the vessel above the liquid would be inconsiderable. The liquid was boiled until a certain temperature was reached. The vessel was then removed, partially cooled, and weighed. This was done at every half-degree. In the table the temperatures are deduced at which boiling occurs in strengths rising 5 per cent. from 20 per cent. In column II. the results are smoothed out under the assumption that there is a rise of  $1^{\circ}211$  for every 5 per cent.

TABLE LVII.

Per cent.	I.	II.
20 . . . .	$101^{\circ}50$	$101^{\circ}50$
25 . . . .	$102^{\circ}83$	$102^{\circ}72$
30 . . . .	$103^{\circ}41$	$103^{\circ}93$
35 . . . .	$104^{\circ}02$	$105^{\circ}14$
40 . . . .	$104^{\circ}50$	$106^{\circ}35$
45 . . . .	$106^{\circ}56$	$107^{\circ}56$
50 . . . .	$107^{\circ}22$	$108^{\circ}77$
55 . . . .	$108^{\circ}85$	$109^{\circ}98$
60 . . . .	$110^{\circ}16$	$111^{\circ}19$
65 . . . .	$110^{\circ}81$	$112^{\circ}40$
70 . . . .	$113^{\circ}00$	$113^{\circ}51$
75 . . . .	$114^{\circ}92$	$114^{\circ}92$

The last of them is saturated at  $\cdot758$  millim. atmospheric pressure, and the result is inserted in the table, § 252.

§ 254. When a conception such as the above is once fairly grasped, numerous exemplary phenomena which have hitherto been vaguely entertained re-present themselves and claim kindred with it. Thus it is well known that the temperatures of fusion of many organic solids are notably lowered when in contact with water, or even when imperfectly dried; and this is more marked with those whose temperatures of fusion are not high, and which are nominally classed among insoluble bodies. Such bodies will, especially when in a state of fine division, condense water from the air, and hold it with such tenacity that they will not relinquish it wholly and immediately when heated to or even above  $100^{\circ}\text{C}$ . Again, acetate of potassium in solution and subjected to heat, shows continuity of the liquid condition between strong solution and anhydrous fusion. Further, if nitrate of ammonium be dried before a brisk fire, or *in vacuo* over sulphuric acid, it has no associated water. But a solution of that salt in water passes, on evaporation over the flame, from the state of solution to that of fusion without intermediate solidification. Nay, under such treatment it may begin to decompose before it has become anhydrous. This has, indeed, led some experimenters to conclude that in the dry crystalline state it contains a molecule of water. This has arisen from the two facts—first, that it is hygroscopic in moist air, and, second, that one of the products of its decomposition in the dry state is water. The lowering of the boiling-point of a liquid by admixture with even a very little of another liquid having even a higher boiling-point is a phenomenon of the same order.

§ 255. *Geological bearing of* §§ 249–254.—Just as in the selective formation of what in my last memoir were described as salt-alloys we may have the artificial type of the genesis of many primary rocks and metamorphic modifications, so in the wonderful solubility in or miscibility with water of such alloys and of some salts at high temperatures we may have a no less clear type of the formation of certain volcanic rocks and an explanation of some of their peculiarities. The function of water in affecting rocks has been subjected to a most exhaustive examination by Daubrée. Water, in both its solid and liquid form, is a rock. Under pressure the limit of temperature is not known to which it may be

heated without decomposition, when in contact with bodies saturated with oxygen. Granting that water may have a so-called critical temperature, and range above it when it is heated with bodies which have no physical relationship towards it, still at high pressures it will be compressible as a vapour to a density at least as great as that of liquid water ; and until actual decomposition ensues the physical relationship of the water-molecule with the rock-molecule will remain possibly unchanged. It is true that at the very highest temperatures water appeared to be decomposed ; but this is only when it is unconfined.

Whether the earth's temperature be vastly greater towards its centre than it is near the surface, or whether the observed increase with depth be confined to a mere skin of the earth, there seems to be no reason to suppose that water may not, and does not, exist at the earth's very centre.

If the earth were a sphere of liquid having a density of 5, the pressure at its centre would be over three million atmospheres—a pressure competent to preserve the density of water at a temperature sufficient to fuse perhaps the most refractory known rocks. But at this high temperature the water would, judging by analogy, mix freely with the rock and relieve itself—one cannot yet say how much (compare, however, my next memoir, IX.), but certainly very greatly from its tension.

That there are true sedimentary formations of course no one can deny ; but to attribute to marine influence the formation of rocks because water is found within them, or because water is liberated when melted rock-masses are ejected, is a contention no longer supportable. Obsidian melted and under pressure will, I presume, mix freely with water. When this pressure is gradually removed, water-vapour escapes, and although it takes with it a large amount of heat, the temperature of the obsidian may still remain above its point of anhydrous fusion, or it may be maintained fused by heat from other sources. Finally cooled, it is the familiar glassy amorphous mineral. A quick release of pressure entails a quick vaporization of water and a quick loss of heat. The obsidian mass, during and because of the loss of water and the loss of heat, becomes pasty and “ rises ” like dough



during fermentation, and becomes pumice, which is often found overlying obsidian. A quicker release of pressure from above causes the vesicular and vesiculating masses to be projected, and if the vesiculation is carried far and fast volcanic dust is produced. That water is one of the accompaniments of volcanic activity is well known. The presence of hydrochloric acid in the ejecta, and the almost universal neighbourhood of the sea to active volcanoes, has favoured the view that the material for the motive power is supplied by the marine irruption. Without entering upon the question as to whether sea-water is essential to volcanoes, and whether hydrochloric acid is a product of the action of acid silicates or silicic acid upon the chlorides in that liquid, I contend that the evidence is conclusive that at one period the melting masses contain water. They are in the same predicament as the nitre liquified along with water at a high temperature and under corresponding great pressure.

This subject has been so fully discussed by Daubrée in his various memoirs, and is so ably treated in his *Géologie Expérimentale*, that, as far as their geological bearing is concerned, my experiments may be considered as merely adding another chapter to his work.

Graham has shown how alumina, silica, oxide of tin, and oxide of iron may be obtained in aqueous solution in the colloidal state; and Daubrée has proved that at high temperature and under pressure water disintegrates and decomposes certain rocks, and rearranges their constituents, and has argued that, assisted by capillarity and high temperature, many phenomena of volcanism and metamorphism are to be attributed to that agent. He has thus vastly extended the scope of the long-known action of water on silicates, and showed that under conditions of temperature water alone plays as potent a part in such disintegration as the fixed alkalies were known to do under like conditions. My experiments may perhaps be considered as leading us a step further. For they show that water at a high temperature may not only play the part of a solvent in the ordinary restricted sense, but that there is in many cases no limit to its solvent faculty; in other words, that it may be miscible with certain rocks in all proportions: that solution and mixture are con-

tinuous with one another. And this continuity, as my experiments prove, is established in some cases,—and these indeed with bodies having no chemical affinity with water,—at temperatures not above the temperatures of fusion of those bodies *per se*. This induces me to think that the replenishment of water in rocks by capillarity, an action upon which Daubree lays great stress and with regard to which he adduces many striking experiments, is not an essential condition. I must, however, leave the discussion of this question to petrologists.

[NOTE added June 16, 1884.—Since the above was in print I have been favoured with a copy of a most interesting memoir by Prof. Tilden and Mr. W. A. Shenstone on the “Solubility of Salts in Water at High Temperatures,” read before the Royal Society of London, June 21, 1883 (Transactions of the Royal Society, Part I. 1884). Accordingly, wherever in the two memoirs there may be found similarity in results or ideas, the priority is theirs.

These gentlemen have apparently been to a considerable extent guided by the conception that there is a relationship between the solubility of a salt in water and its temperature of fusion. And perhaps their main argument concerns this relationship. They have made a special study of those interesting cases in which the solid salt contains water of crystallization. This branch of the inquiry I have rather deliberately avoided, as I wished to establish the analogy between metallic and dry-salt alloyage, on the one hand, and water-salt alloyage on the other. Nevertheless they examined the solubility of nitre in water at 125°. Their experiments on solubility appear to stop short far below the temperature of fusion of the salt *per se* (excepting in cases where the salt contains water of crystallization). They distinctly state, however, that infinite solubility is “nearly true of benzoic acid, which melts at 120°. . . . . By sealing it up with water in a glass tube and heating to a few degrees beyond the melting-point, intermixture occurs in all proportions; and the liquid so obtained, on cooling to 120°, or about 1° lower, becomes turbid from deposition of oily drops, which, however, immediately crystallize.” —F. G.]

**XV. *On a new Apparatus for Colour-Combinations.* By H. H. HOFFERT, B.Sc., A.R.S.M., Assistant in the Physical Laboratory, South Kensington\*.**

[Plate XI.]

VARIOUS arrangements for the mixture of colours have already been devised by Maxwell, Rayleigh, Helmholtz, and others, by means of which the laws of colour-combinations have, in their main features, been firmly established.

Wishing to observe for myself the principal phenomena connected with this subject, I have repeated, during the past winter, many of the experiments thus described, both with the colour-top and with overlapping spectra. Being desirous of obtaining some convenient arrangement whereby any two or three colours of the spectrum could be combined in any required proportion, and compared with the colours either of natural objects or of other spectral combinations, I tried various experiments, using the method first adopted by Maxwell, of observing, by means of a slit-eyepiece, the spectra produced by light proceeding from illuminated slits, and passing through a train of glass prisms; this method being equivalent to looking through a hole in a screen on to which are cast two or three superposed spectra, so that the colour perceived is that due to the mixture of those parts of the several spectra which fall on the hole.

In these experiments I have been assisted by my colleague Mr. Mitchell, to whom I am also indebted for several valuable suggestions.

We first tried a modified form of Maxwell's colour-box, using eventually six equilateral glass prisms, arranged in two sets of three symmetrically with respect to the eyepiece; so that if the latter be made a source of light, the rays are bent through about  $150^\circ$ , and being then received on to a lens, are focused on to planes situated on either side of the eyepiece, this arrangement being found very convenient for manipulation.

Movable slits of fixed width, sliding in a frame with bellows-screens of opaque silk between, were used as sources of light,

\* Read June 14, 1884.



lamps being placed outside them. The intensity of the light was regulated by means of Nicol prisms, one being attached to each slit, so as to be capable of rotation, while an analyzing Nicol was fixed in the eyepiece. The intensity could thus be readily altered for each slit separately.

This arrangement was found to answer fairly well, but its necessarily large dimensions were a great inconvenience. A very long spectrum was needed, as the slits could not be brought very close on account of the size of the Nicol prisms; hence also there was great loss of light.

Movable slits, whether of fixed or adjustable width, are very troublesome to manipulate, and do not admit of very rapid and easy adjustment; they were therefore abandoned altogether, and in their place the light from small lengths of platinum wire, heated to incandescence by an electric current, was employed. Preliminary trials having proved satisfactory, the apparatus was constructed which I now bring before your notice.

The prisms, lenses, and sources of light are enclosed in a flat box of irregular hexagonal shape, at the smaller end of which the six prisms (P, Pl. XI.) are placed. These are arranged, as already described, in two sets of three, each prism being set to minimum deviation. The first prisms have their refracting-edges in contact; and by means of a screen (S), in which is a small rectangular aperture, small equal strips of the adjacent faces of these prisms are visible from the eyepiece (E), which is a small brass tube with a narrow slit, about  $\frac{1}{16}$  inch wide.

Supposing light to come from the eyepiece, the prisms would deflect it through about  $150^\circ$ ; it would then fall on to two lenses (L), of about 10 inches focal length, which focus the spectra on to the two sides of the box immediately to the right and left of the eyepiece. Here are placed the incandescent wires (W); so that, conversely, if these be the sources of light, the rays follow an inverse course, and the corresponding half of the aperture in the screen is seen illuminated with a colour which will depend on the position of the incandescent wire, and which will be pure and uniform if the wire be not too thick, the slit in the eyepiece too wide, or the strip of the prism exposed too large. The colours are found in practice to be perfectly uniform.

The prisms and lenses are supported at the level of the incandescent wires, on a horizontal floor (G), which divides the box two inches from the top into two compartments, and which is cut away so as to leave a space for the tops of the frames carrying the wires to enter the upper compartment. These frames (W), which are six in number, three on each side, consist of brass wires held on small ebonite blocks (I), which slide along a steel rod (H) supported on a ledge inside the box. The frames can be moved along the length of the spectrum from outside by means of openings (A) cut in the sides of the box, into which the hands can be introduced. These openings are below the level of the horizontal floor, so that the upper compartment, which is everywhere blackened inside, is quite impervious to external light, unless the lids in the cover of the box, to be presently described, are opened.

The frames are connected by flexible wires to a series of resistances arranged in the lower compartment of the box; and by means of six dials (R), on the sides of the box, each of the six circuits can be altered in resistance at will, so that the incandescent wires can be rapidly adjusted, whether in position or in intensity, by the observer without his having to remove his eye from the eyepiece. Six pairs of binding-screws (T) at the back of the box connect the six circuits with a Grove battery. By this means, when the current is passing, the aperture in the screen is seen divided into two coloured strips in close juxtaposition; one colour being that due to the wires and prisms on the right hand, the other to those on the left. The colours can thus be readily compared and adjusted to exact identity.

It remains to describe the means by which external colours can be introduced for comparison with those produced by the prisms.

The cover of the box contains three small hinged lids. Two of these (C) are over the luminous wires, and serve to adjust or replace the wires in case of accidental fusion. The third lid (D) opens over the space just in front of the screen. Here is placed a small strip of microscope cover-glass (M), inclined at about  $60^\circ$  to the horizontal, and so arranged that, as seen from the eyepiece, it exactly covers that portion of the aperture in the screen which is illuminated by the light from the

left-hand train of prisms, this light being thus seen through the glass slightly diminished in intensity. On the underside of the lid is a small silvered mirror (N); and by raising the lid to the proper height, the colour of any object laid on the top of the box is seen by double reflection in the eyepiece, exactly coinciding with the left half of the aperture in the screen. This colour may be either combined with that from the left-hand train of prisms, or compared with that from the right-hand train. For white light I use the light from a window, which may be reduced in intensity to any desired amount by passing it through one or more pieces of roughened glass, held in a frame placed on the top of the box. Coloured glasses, or cells of coloured fluids, can similarly be placed in the frame, so that almost every possible combination or comparison of colours may be made. Another frame, which may be placed inside the box between the screen and the eyepiece, serves to show the action of different absorbing media on colours identical in appearance but of different composition.

The colours produced are uniform, very constant, and fairly bright. Those from the blue and violet parts of the spectrum are necessarily more deficient in luminosity. This is partially compensated by using in the less luminous parts of the spectrum ribbons of platinum, produced by rolling out the wires, with their flat surfaces turned towards the lenses. This is equivalent to increasing the width of the slit in ordinary arrangements. Should the wires become fused through incautiously using too strong a current, they can be very readily replaced by means of the screws (K).

For the current, three Grove's cells are needed for each of the ribbons and two for each of the wires. But since the frames carrying the wires can be brought together till the wires are nearly in contact, and since the wires themselves offer extremely narrow luminous surfaces, a very long spectrum is not needed; and by using more powerful lenses and bringing the sliding frames closer to them, a greater intensity of light would result; while the size of the box might thus be reduced to one half or even less of its present amount, the eyepiece being kept at a sufficient distance by the use of a longer tube, which might be made removable. One Grove



cell would then suffice for each wire, or at most two when experimenting on the violet rays.

Instead of the step-by-step dial-resistances, some arrangement giving, like the rheostat, a gradual adjustment of the intensity would be perhaps preferable.

Scales can be attached in front of the sliding frames to show the exact position in the spectrum of each of the luminous wires.

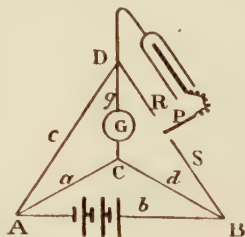
I trust that the ease and rapidity with which the adjustments in this apparatus can be made will cause it to be found useful in those many cases in which it is impossible or inconvenient to make use of the more powerful effect of direct sunlight.

XVI. *On a Method of Measuring the Electrical Capacity of a Condenser, and on the Determination by Electrical Observations of the Period of a Tuning-fork.* By R. T. GLAZEBROOK, M.A., F.R.S., Demonstrator of Experimental Physics at the Cavendish Laboratory, Cambridge\*.

THE experiments described in the following paper were undertaken at the request of Messrs. Latimer Clark, Muirhead, and Co., for the purpose of testing one of their condensers "which," quoting from a letter from the firm, "has lately been made and which we use in the factory. In its construction it is the same as all our condensers, and is made of sheets of mica and tinfoil and laid with paraffin-wax."

The method employed was a modification of one given by Maxwell (vol. ii. § 776), and used by J. J. Thomson (Phil. Trans. iii. 1883) in his recent determination. The following is his description of the arrangement:—

"In a Wheatstone bridge, A B C D (fig. 1), with the galvanometer at G and the battery between A and B, the circuit B D is not closed, but the points B and D are connected with two poles, R and S, of a commutator, between which a travelling piece, P, moves backwards and forwards. P is connected with one plate of a condenser, the other plate of which is connected



\* Read June 28, 1884.

with D. Thus, when P is in contact with S the condenser will be charged, and until it is fully charged electricity will flow into it from the battery: this will produce a momentary current through the various arms of the bridge. When the moving piece P is in contact with R, the two plates of the condenser are connected, and the condenser will discharge itself through D R; and as the resistance of D R is infinitesimal in comparison with the resistance in any other circuit, the discharge of the condenser will not send an appreciable amount of electricity through the galvanometer. Thus, if we make the moving piece P oscillate quickly from R to S, there will, owing to the flow of electricity to the condenser, be a succession of momentary currents through the galvanometer. The resistances are so adjusted that the deflection of the galvanometer produced by these momentary currents is balanced by the deflection due to the steady current, and the resultant deflection is zero. When this is the case, there is a relation between the capacity of the condenser, the number of times the condenser is charged and discharged in a second, and the resistances in the various arms of the bridge."

The investigation given by Maxwell is only approximate; we shall quote therefore the result given in Thomson's paper.

Let  $a$  be the resistance of A C,

$b$         "        "        A B,

$c$         "        "        A D,

$d$         "        "        B C,

$g$         "        "        D C.

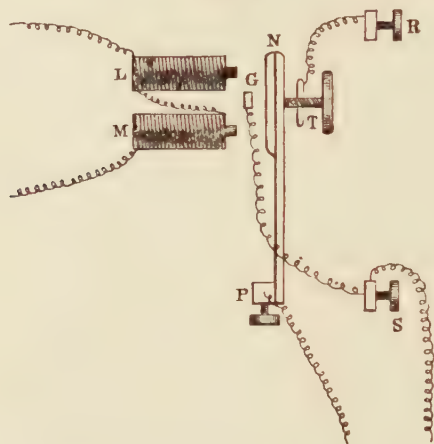
Let  $C$  be the capacity of the condenser,  $n$  the number of times it is charged and discharged per second; then

$$nC = \frac{a \left\{ 1 - \frac{a^2}{(a+c+g)(a+b+d)} \right\}}{cd \left\{ 1 + \frac{ab}{c(a+b+d)} \right\} \left\{ 1 + \frac{ag}{d(a+c+g)} \right\}}.$$

The commutator was the one used by J. J. Thomson, and we will quote his description:—"The current from some Grove cells passes first through a tuning-fork interrupter and

then through the coils L M (fig. 2) of an electromagnet. P N is a strip of brass with a piece of iron wire attached to it

Fig. 2.



When there is no current passing through the electromagnet the elasticity of the rod P N makes it press against the screw T, which is electrically connected with the binding-screw R. When the current passes through the electromagnet, the magnet attracts the iron attached to the rod P N and brings it into connexion with the stop G, which is electrically connected with the binding-screw S. The letters P R S indicate the same points in this figure as in fig. 1. All the places where contact is made are covered with platinum, and the whole arrangement is fastened down to an ebonite board. As the current passes intermittently through the coils L M of the electromagnet, the vibrating-piece P N strikes alternately against the parts G and T. When it strikes against G, the opposite plates of the condenser are connected with the two poles of the battery; when it strikes against T, the condenser is discharged."

The main advantages of this method over the one ordinarily employed for the determination of the capacity of a condenser whose capacity is comparable with a microfarad are easily seen. In the first place it is a null method; no assumptions are required as to the constancy of the battery. In the

second, the galvanometer can readily be made much more sensitive. For accurate work in the ordinary method, the field of force in which the galvanometer-needle hangs should be nearly uniform. The earth's force is much too strong, unless an enormous battery-power be employed, and it is difficult to secure a uniform field by a control magnet. Something may of course be done by the use of an astatic galvanometer-needle; but it is impossible to increase the sensitiveness in this way very much, because the torsion of the suspending fibre then becomes important. Again, in the ordinary method the time of swing cannot be determined accurately if it be made too small; the moment of inertia of the suspended parts therefore must be considerable, and the deflection produced by a given quantity of electricity suddenly discharged through the galvanometer is proportionately decreased; for, if  $T$  be the time of swing,  $\theta$  the throw produced by a quantity of electricity  $Q$ , then  $T \sin \frac{1}{2} \theta$  is proportional to  $Q$ . In addition to this, there is the correction for damping which has to be considered.

On the other hand, objections may be raised to the method which has just been described. The most important of these is founded on the fact that the time during which the plates of the condenser are in contact either with each other or with the poles of the battery is very short. It may happen, then, that the condenser is neither charged nor discharged completely at each vibration of the commutator; while if there be any electrical absorption in the condenser, its effects will depend on the time during which the contact lasts. The experiments to be described were undertaken with the view of testing the method for these defects. The time during which the plates of the condensers are connected with the battery is the time during which the spring  $PN$  is in contact with  $G$ . This is only a fraction of the period of the tuning-fork which governs the commutator, a fraction which depends on the distance between the end of the screw  $T$  and the point  $G$ , and on the strength of the current in the electromagnet.

A series of experiments were made to test the effect of varying the position of the screw  $T$ , keeping the battery the same. In these, four Leclanché cells were used in the battery-circuit  $AB$ , and two pint Groves to drive the commutator.



The position of the spot of light on the scale was noted, and then the value of the resistance  $d$  adjusted until no deflection was produced when the galvanometer-circuit was closed by means of a key.

The commutator, when working correctly, emitted a definite sound which was readily recognized; and it was found that the screw T could be adjusted within certain limits without altering this sound.

Table I. gives the results of these observations.

TABLE I.		Value $d$ in B.A. units.
Commutator adjustments.		
Screw T set.....		905
Screw T readjusted, note good .....		906
"        "        "        " .....		906
"        "        "        bad .....		906
"        "        "        good .....		906
Screw T loosened one turn.	Spot off scale.	
Screw T readjusted, note good .....		906

Thus the value of  $d$  required to give a balance is practically the same throughout, and the commutator with a definite battery-power can readily be set to give a definite result; moreover, a balance could never be obtained except with the resistance 905 or 906. In the fourth observation the note of the commutator was marked as bad; but the spot remained stationary, showing that though there seemed to be a slight irregularity in the sound, it was too small to affect the balance. The sensitiveness was such that an alteration in  $d$  of 1 B.A. unit produced a deflection of from two to three scale-divisions. The number of vibrations of the fork was about 32 per second.

Another set of observations was then taken to test the effect of varying the battery-power driving the commutator, thus altering the force with which the spring P N is attracted to G, three Grove cells being used in place of two. The values of  $d$  found in two separate observations were 905.5 and 905.

Observations were made to test the effect of varying the period of the driving-fork. Forks of frequencies of

approximately 16, 32, 64, and 128 to the second were taken, and the pitch of the lowest of these determined absolutely by comparison with the clock in the method described by Lord Rayleigh ('Nature,' xvii. p. 12; Phil. Trans. 1883, Pt.I.). This fork and the 32 fork were then set going on independent circuits, and a pointer attached to the 32 fork was watched over the top of a plate of thin metal which had been all along fixed on to the 16 fork, the eye being placed so that this pointer was visible for only one position of the 16 fork in each vibration. In this way the beats between the octave of the 16 fork and the 32 fork were visible, and could easily be counted.

Thus the period of the 32 fork was found, and then in a similar manner those of the 64 and 128 forks. By loading with wax one of the two forks under comparison, it was easy to find which of the two was gaining.

Each of these forks was used in turn to drive the commutator, and the value of the capacity calculated from the observations. The values of the resistances were as follows:—

$a$  was a standard coil of 10 B.A. units,  $d$  a resistance of 1000 B.A. units, taken from a box by Messrs. Elliott, Bros., and  $c$  a variable resistance from another box by the same firm.

$g$ , the galvanometer-resistance, was about 11,000 B.A. units; and  $b$ , the battery-resistance, from 5 to 6 B.A. units. The galvanometer-resistance was higher than necessary, but it was for other reasons the most convenient instrument for the purpose. The value of  $c$  varied from about 1800 to about 240 B.A. units.

It will be found that, with these values, the equation giving the capacity may be written

$$nC = - \frac{a}{cd \left\{ 1 + \frac{a}{d \left( 1 + \frac{c}{g} \right)} \right\}}.$$

[The approximate equation given in Maxwell is

$$nC = \frac{a}{cd}.]$$

We shall use  $N_{16}$  &c. to denote the frequency of the fork of approximate frequency 16.

The following are the results of the observations :—

(1) Fork 16 used.

Fork compared with pendulum. Fork loses 1 vibration in 7.46 seconds.

$$N_{16} = 15.866 \text{ sec.}$$

Resistance observation :—

$$a = 10; \quad d = 1000; \quad c = \left\{ \begin{array}{l} 1895 \\ 1892 \\ 1893 \end{array} \right\} 1893 \text{ mean.}$$

Sensitiveness 1 scale-division for alteration of 1 B.A. unit in  $c$ .

From these we find

$$C_{16} = .3300 \frac{\text{ohm}}{\text{B.A. unit}} \text{ microfarad.}$$

(2) Fork 32 used.

16 beats occur in 42 seconds between octave of 16 and 32. Fork 32 gaining.

$$N_{32} = 32.11.$$

Resistance observations :—

$$a = 10; \quad d = 1000, \quad c = \left\{ \begin{array}{l} 934 \\ 934 \\ 934 \end{array} \right\} 934 \text{ mean.}$$

Hence

$$C_{32} = .3304 \frac{\text{ohm}}{\text{B.A. unit}} \text{ microfarad.}$$

(3) Fork 64 used.

10 beats occur between 64 and octave of 32 in 50 seconds. Fork 64 gaining.

$$N_{64} = 64.42.$$

Resistance observations :—

$$(\alpha) \quad a = 10; \quad d = 1000; \quad c = 466;$$

$$C_{64} = .3299 \frac{\text{ohm}}{\text{B.A. unit}} \text{ microfarad.}$$

$$(\beta) \quad a = 10; \quad c = 1000; \quad d = \left\{ \begin{array}{l} 461 \\ 461.5 \end{array} \right\} 461.3 \text{ mean.}$$

$$N_{64} = .3299 \frac{\text{ohm}}{\text{B.A. unit}} \text{ microfarad.}$$

(4) Fork 128 used.

16 beats occur between the 128 fork and octave of 64 fork in 26.25 seconds. Fork 128 gaining.

$$N_{128} = 129.05.$$

Resistance observations:—

$$a=10; \quad d=1000; \quad c=232\cdot5.$$

Hence

$$C_{128} = \cdot3301 \frac{\text{ohm}}{\text{B.A. unit}} \text{ microfarad.}$$

The sensitiveness throughout these observations was such that an alteration of 1 in 2000 in the resistance produced a deflection of about one scale-division in the spot of light.

Hence the greatest difference in the observations amounts to about 5 in 3300, or about 1 in 660; and there is no trace visible of variation in the capacity with the time of charging.

We will collect the numbers together:—

$C_{16}$ .....	$\cdot3300$
$C_{32}$ .....	$\cdot3304$
$C_{64}$ .....	$\cdot3299$
$C_{64}$ (second arrangement).....	$\cdot3299$
$C_{128}$ .....	$\cdot3301$

$$\text{Mean value of capacity} = \cdot33006 \frac{\text{ohm}}{\text{B.A.U.}} \text{ microfarad.}$$

Taking the Cavendish-Laboratory experiments, we have

$$1 \text{ B.A. U.} = \cdot9867 \text{ ohm.}$$

$$\begin{aligned} \therefore C &= \frac{\cdot33006}{\cdot9867} \text{ microfarad} \\ &= \cdot3344 \text{ microfarad.} \end{aligned}$$

If we take the legal ohm and the value of the specific resistance of mercury in B.A. units, adopted by the B.A. Committee,

$$1 \text{ B.A. unit} = \cdot9889 \text{ ohm,}$$

and

$$C = \cdot3336 \text{ microfarad.}$$

This value supposes that the various coils used have their nominal resistance in B.A. units. And this assumption is correct, at any rate to 1 in 1000. Thus it seems that the method gives satisfactory results, and may safely be used to determine the capacity of a condenser.

But the converse of the method may be even more useful. The fundamental equation gives us  $C$  if we know  $n$  and the resistances; it will equally give us  $n$  if we know  $C$  and the resistances; and in many cases this may be the readiest



method of finding  $n$ , especially if the period is too long to give an audible note. Thus in the above experiments I require to adjust a fork to vibrate about 16 times a second, the lowest I could obtain being one of a frequency of almost 20.

I made observations with the 32 fork, the pitch of which was marked on it by the maker, of the value of  $c$  required to produce a balance, then doubled this value of  $c$ , and set the fork which it was required to adjust to drive the commutator. Lead weights were then fixed with screws on to the prongs of the fork, and their position was adjusted until the galvanometer-balance was not disturbed on making contact. It was clear, then, from the approximate formula that the frequency of the fork was very nearly 16. And on making the comparison with the clock, it was found to be 15.866, as already stated.

My thanks are due to Messrs. Wilberforce, Whitehead, and Fitzpatrick for assistance in making the experiments.

## XVII. *On the Thermal Relationship between Water and certain Salts.* By B. ILLINGWORTH and A. HOWARD\*.

THE study of the relationship towards water of certain organic salts belonging to one and the same series promised to throw light upon the general question of the relationship between salts and water, inasmuch as the *degree* of difference between the members compared may be made at will very considerable; while the *kind* of difference is not to be compared with that resulting from the substitution of an acid or basic element in a given salt.

We have accordingly submitted to examination the sulphomethylate, the sulphoethylate, and the sulphoamylate of potassium ( $K, CH_3 SO_4$ ;  $K, C_2 H_5 SO_4$ ; and  $K, C_5 H_{11} SO_4$ ): and we venture to think that the results are of sufficient interest for us to give the following brief account of them.

We satisfied ourselves that the substances were nearly pure. The methyl salt contained, however, a trace of chlorine, and the amyl salt was not quite free from the same impurity. They were finely powdered, and dried over sulphuric acid in

\* Read June 14, 1884.

partial vacuum until they ceased to lose weight. A thermometer, the error of which at  $0^{\circ}$  was determined, and which was graduated to tenths of a degree (each tenth being  $\frac{1}{10}$  millim. long), enabled us to read temperatures with considerable precision.

*Sulphoethylate of Potassium* ( $K, C_2 H_5 SO_4$ ).—Starting with the ethyl salt, a preliminary examination, made by mixing the salt with about twice its weight of finely crushed ice, showed the cryogen value to be  $-13^{\circ}.9$  C. This, according to analogy, should be the melting- and solidifying-temperature of the cryohydrate. Solutions containing various percentages of the anhydrous salt were made and submitted to a salt-ice cryogen, the temperature being noted at which solidification began.

With regard to the solubility at the air-temperature:—A solution saturated at  $21^{\circ}$  C. was allowed to cool for several hours until it reached  $15^{\circ}.1$  C. Of this solution, 7.3342 grams were weighed in a covered basin and then dried *in vacuo* over sulphuric acid. The nearly dry mass was powdered and redried until it ceased to lose weight. 4.5732 grams, or 62.35 per cent., were thus obtained.

A solution saturated at the air-temperature was fairly buried in melting ice for several hours and until its temperature had remained for a few hours at  $0^{\circ}$  C. Examined as above, 24.0880 grams gave 12.9375 grams of anhydrous salt, or 53.71 per cent.

A solution of strength between 40 and 50 per cent. was cooled in an ice-salt cryogen until its temperature remained constant at  $-14^{\circ}.2$  C. After a considerable amount had solidified, 11.9813 grams of the solution were dried, and yielded 5.3932 grams dry salt, or 45.01 per cent. It will be noted that the temperature of the cryogen of this salt was found to be  $-13^{\circ}.9$ , or  $0^{\circ}.3$  higher than the melting-point of the cryohydrate.

TABLE of Sulphoethylate of Potassium and Water.

Sulphoethylate of potassium, per cent.	Water, per cent.	Temperature at which solidification begins.	Body separated.
10	90	- 2.2	Ice.
20	80	- 4.9	"
30	70	- 8.2	"
40	60	- 12.1	"
45.01	54.99	- 14.2 (cryogen - 13° 9)	Cryohydrate.
50	50	- 6 (interpolated)	Salt.
53.71	46.29	0	"
62.35	37.65	+ 15	"

*Sulphomethylate of Potassium* ( $K, CH_3 SO_4$ ).—The mode of procedure was precisely like that above described.

As a cryogen, it showed a temperature of  $-11^{\circ} 3$ .

At the air-temperature ( $12^{\circ} 3$ ) an amount of 5.2254 grams gave 2.8654 grams residue, or 54.8 per cent.

16.5250 of the solution saturated at  $0^{\circ}$  gave 2.8654, or 47.08 per cent.

The solidifying-temperature of the cryohydrate was found to be  $-11^{\circ} 8$ ; and 9.4940 grams of it yielded 3.7824, or 39.84 per cent. anhydrous salt.

TABLE of Sulphomethylate of Potassium and Water.

Sulphomethylate of potassium, per cent.	Water, per cent.	Temperature at which solidification begins.	Body separated.
10	90	- 2.3	Ice.
15	85	- 3.6	"
20	80	- 5.0	"
30	70	- 8.0	"
39.84	60.16	- 11.8 (cryogen - 11° 3)	Cryohydrate.
40	60	- 11.5 (interpolated)	Salt.
47.08	52.92	0.0	"
54.8	45.2	+ 12.3	"

*Sulphoamylate of Potassium* ( $K, C_6 H_{11} SO_4$ ).—This salt \*, on being treated in quite a similar manner, gave the following results.

The temperature of the cryogen was found to be  $-5^{\circ} C$ .

At the air-temperature ( $17^{\circ} 3$ ), a solution weighing 6.8099 grams gave 4.0494 grams residue, or 59.46 per cent.

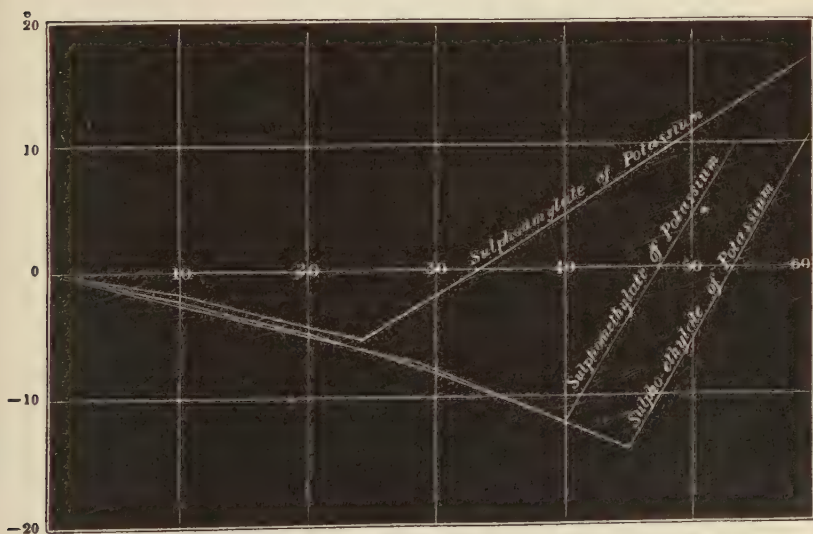
\* Probably isoamylate.

The solidifying-temperature of the cryohydrate was found to be  $-5.4$ ; and 11.958 grams of it gave 2.8737 grams of anhydrous salt, or 24.03 per cent. 15.667 of the solution, saturated at  $0^{\circ}$ , gave 5.240 of anhydrous salt, or 33.44 per cent.

TABLE of Sulphoamylate of Potassium and Water.

Sulphoamylate of potassium, per cent.	Water, per cent.	Temperature at which solidification begins.	Body separated.
10	90	$-1.9$	Ice.
20	80	$-4.3$	"
24.03	75.97	$-5.4$ (cryogen $-5^{\circ}$ )	Cryohydrate.
25	75	$-4.8$ (interpolated)	Salt.
33.44	66.56	$0.0$	"
59.46	40.54	$+17.3$	"

The accompanying figure shows the relationship, in respect to water, of these three closely allied salts. The abscissæ are percentages, the ordinates temperatures.



The ethyl and methyl combinations run an almost common course as far as the cryohydrate of the latter. They cross at about 24 per cent. The cryohydrate of the ethyl salt contains about 5 per cent. more salt and melts at  $2.4$  lower. The



ascending or salt branches of the curves are almost absolutely parallel, but exhibiting a slightly opposite curvature.

Perhaps the most salient fact concerning this group is that the methyl compound is intermediate in these of its physical properties between the ethyl and the amyl members. So interesting did this relationship appear, that we have determined the specific gravities of the three salts. Turpentine was used as the liquid displaced. The dry salt having been weighed in the specific-gravity bottle, a little turpentine was added and the air exhausted. The bottle was subsequently filled with turpentine in the usual way. The air-temperature was  $19^{\circ}\cdot6$ , and the specific gravity of the turpentine compared with water at the same temperature was  $0\cdot86838$ . It was found that

at $19^{\circ}\cdot6$	{	sp. grav. of sulphomethylate of potassium	= $2\cdot097$ ,
		„ „ sulphoethylate of potassium	= $1\cdot843$ ,
		„ „ sulphoamylate of potassium	= $1\cdot144$ .

Accordingly the densities of the salts are in the inverse order of their molecular weights, and the ethyl compound is in this respect in its usual place between the amyl and methyl relatives.

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### XVIII. *Preliminary Notice of a new Sunshine-Recorder.*

*By* HERBERT M'LEOD, *F.R.S.\**

BEING somewhat doubtful of the accuracy of the published reports of the duration of sunshine, in the summer of 1880 I tried to devise some apparatus by which the light, instead of the heat of the sun, would be used to produce the record of sunshine. Several trials were made; and in some of them clockwork was employed to move strips of sensitive paper. The simplest form of apparatus I have recently tried again, using the ferroprussiate paper now much employed by engineers for copying tracings, and which is preferable to silver paper, first, in consequence of its

\* Read June 28, 1884.

cheapness, and, secondly, because of the ease with which the image is fixed, as for this purpose washing in water is sufficient.

The apparatus consists of a camera so fixed that its axis is parallel to the polar axis of the earth, the lens pointing northwards. Opposite the lens a silvered sphere is placed. The rays from the sun are reflected from the sphere through the lens of the camera on to the sensitive paper, on which a distorted image of the sun is formed ; and the positions of the lens and sphere are so arranged that the image is a linear one and radial. By the motion of the earth the image is carried round in a circular arc, tracing a curve on the sensitive paper. In the instrument at present constructed, the sphere is a chemical round-bottomed flask silvered inside, and about 95 millim. in diameter ; the distance from flask to lens is 76 millim., and from lens to sensitive paper 152 millim. ; the lens has a focal length of 90 millim. and an effective aperture of 22 millim.

The circle traced by the sun in June is about 120 millim. in diameter. An impression is made on the paper by exposure for only 10 seconds ; and when the lens is covered for one minute, a light line is produced in the circular band, so that the paper is sufficiently sensitive in the present apparatus to register short gleams of sunshine, and also the passage of small clouds. When the sun is shining through light clouds, an impression is produced on the paper, but somewhat blurred, and of a much less intense blue colour than is obtained by bright sunshine. The time-scale is made by drawing from the centre of the circular band radial lines, containing between them angles of  $15^{\circ}$ , each of which represents one hour of time.

It still remains to be found which are the most convenient dimensions for the globe and lens, so that the minimum of alteration of position will be requisite to obtain a sharp image during all times of the year ; and also the best method of fixing the paper so that it may be easily changed and the time-scale marked on it.

XIX. *A Magneto-electric Phenomenon.* By C. V. BOYS,  
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EVERY one is familiar with the effect produced when a copper disk is set to spin in a powerful magnetic field : the currents induced by the motion of the disk act in such a direction as to oppose the motion, which therefore speedily ceases. Faraday observed that if, instead of being set to spin, a disk is merely suspended between the poles of an electromagnet, it will in general be disturbed whenever the current in the coils of the electromagnet is made or broken. If it lie with its plane parallel or at right angles to the lines of force, no disturbance will be apparent if the lines of force where they are included by the disk are parallel. But if the plane of the disk makes an angle  $\alpha$  with the parallel lines of force, then on making the current in the electromagnet an impulse is given tending to diminish the angle  $\alpha$ , while breaking the current gives an impulse tending to increase the angle  $\alpha$ .

Again, if the angle  $\alpha$  be  $90^\circ$ , so as to eliminate this twisting effect, no movement will be visible at the making or the breaking in a parallel field ; but if the disk be placed in a field with diverging lines of force, in which, of course, the strength diminishes as the lines separate, and if it be placed symmetrically so as to include the greatest number (*i. e.* with its plane at right angles to those lines passing through its centre), then, on making the current, it will receive an impulse causing it to move parallel to itself along the lines of force towards the weaker part of the field, and at the breaking it will receive an impulse more evident in the opposite direction. If this radiating field is produced between a pointed and a flat pole, the disk will, on making the current, appear to be repelled from, and, on breaking, to be attracted by, the pointed pole. So powerful is this effect that a piece of impure copper, which is strongly magnetic, is repelled from the pointed pole on making, and attracted on breaking, the current, thus appearing at first sight strongly diamagnetic.

Though these impulses must have been observed by most

\* Read June 28, 1884.

experimentalists, their amount has not been, so far as I am aware, determined in absolute units, nor have they been turned to account for making any measurements. As they seem to afford one of the most convenient methods of determining conductivity and field-intensity, perhaps a short paper on the subject, even though it be incomplete, may be of interest to this Society.

The explanation of the motions described will be obvious, but it may be well to give it at length for the sake of arriving at quantitative results. In the first place, let the lines of force be parallel, so that the field is of uniform strength. Let a ring of (small) section  $s$ , of specific resistance  $\rho$ , and of radius  $r$ , be placed in the field, with its plane making an angle  $\alpha$  with the lines of force. Let the strength of the field be  $H$  units. Then during a small increment of field-intensity  $dH$ , in the time  $dt$ , a current will be induced in the ring of the strength

$$\frac{rs \sin \alpha}{2\rho} \frac{dH}{dt}.$$

This current in the field  $H$  will produce a twisting tendency to increase  $\alpha$  with a diminishing, or to diminish  $\alpha$  with an increasing field, represented by the couple

$$-\frac{\pi r^3 s H \sin 2\alpha}{4\rho} \frac{dH}{dt}.$$

From this it is clear that the couple varies inversely as the time  $dt$  occupied in making any small change of field-intensity  $dH$ , but it lasts for the time  $dt$ ; therefore the momentum acquired by the suspended disk, if free to move, will be independent of the rate at which any small change in the magnetic field may be made, but will depend only on its amount, provided that the time is not sufficient for the angle  $\alpha$  to have perceptibly altered during the change. Since this is true of any element, it is true of all; so the momentum acquired by the ring is a direct measure of any total change in the strength of the field in which it lies, no matter by what law it changes in strength. If at the end of any rapid change the field remains of any strength, the motion of the ring will be rapidly stopped by the well-known damping action, of which I shall have more to say later. If, however, the field sinks to zero,



or nearly so, the momentum acquired can be measured and the original intensity determined.

The current induced in the ring will of course react on the field and bend the lines of force in such a manner as to hinder their passing through its edge, that is to delay the change of included field-intensity; but the impulse is independent of the time or the manner in which the field changes, so it cannot be effected to any extent by this cause.

Since the impulse given to the disk during any element of time is

$$-\frac{\pi r^3 s H \sin 2\alpha}{4\rho} \frac{dH}{dt},$$

the total impulse while  $H$  changes between 0 and  $H$  will be

$$-\frac{\pi r^3 s H^2 \sin 2\alpha}{8\rho}.$$

If the moment of inertia of the disk be  $M$ , and the torsional value of the supporting wire be  $T$ , the angular velocity  $\omega$  generated will be

$$\omega = -\frac{\pi r^3 s H^2 \sin 2\alpha}{8\rho M},$$

and the throw of the ring  $\theta$  will be

$$\theta = -\frac{\pi r^3 s H^2 \sin 2\alpha}{8\rho \sqrt{MT}}.$$

The action on a disk may be considered as the sum of the actions on the several elementary rings of which it is composed, for there cannot be any tendency for any part of the currents to cross over the elementary circles. The impulse therefore on a disk of radius  $r$  and thickness  $s$  will be

$$-\frac{\pi r^4 s H^2 \sin 2\alpha}{32\rho};$$

and the impulse on a disk of radius  $r_2$  with a concentric hole of radius  $r_1$  will be

$$-\frac{\pi s H^2 \sin 2\alpha}{32\rho} (r_2^4 - r_1^4).$$

Since the moment of inertia of a disk is also proportional to the fourth power and to the thickness, so long as the thickness is small, it will appear that the velocity imparted to a disk of any size or thickness, or to a ring, during a change in a magnetic field will be the same. To what extent a correction should be applied to these results for self-induction between different parts of the disk I am not prepared to say; their calculation would give trouble.

For comparing one field with another, disks or rings of metal may be used; but for absolute measurements, as it would be impossible to measure the exact conductivity of a disk, a coil is preferable. By employing disks of different metals their conductivities can be compared without the trouble of drawing into wire or cutting into long strips.

It will be found that a coil of area  $A$  and resistance  $R$  will, under a torsion  $T$ , experience a throw

$$\theta = - \frac{A^2 H^2 \sin 2\alpha}{4R\sqrt{MT}}.$$

If, instead of a disk, a sphere be used, no twisting should be experienced if the conductivity in different directions is the same. If, however, there is a plane of greatest or least conductivity, it should be possible to discover it. Crystallization or mechanical treatment might give rise to such planes in metals; no definite results could be expected in any thing else.

I have referred to the apparent repulsion and attraction of a disk of metal by a pointed pole at the making and breaking of the magnetizing current. As the lines from such a pole radiate outwards, they are not normal to the metal except in the middle. On their passage inwards or outwards they give rise to circular currents tending to move each part of the disk normally to the lines of force. There is therefore a longitudinal component away from the point of radiation during an increase in the field, and towards it during a diminution of the field. A closed coil of wire is subject to the same forces. If a coil be made of uncovered copper wire in the form of a double helix with the ends joined together, and if the convolutions are separate so as nowhere to touch one another, the growth of the magnetic field can be watched by placing the coil nearly

over one pole. On making the current the field begins to grow, at first quickly and afterwards more slowly. The coil will receive a push and will extend itself. As the push diminishes in amount, owing to the diminishing rate of growth of the magnetic field, the coil will gradually regain its former shape. It might be thought that the slow recoil is simply due to the damping action of the field; but this is not sufficient to account for it, as when the field is fully grown the coil will, on being forcibly drawn out, recover its shape much more quickly. On breaking the magnetizing current, the impulse in the opposite direction, being the same as before but lasting for so much shorter a time, is far more evident.

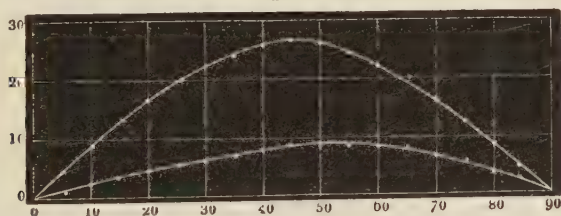
My first experiments were made with a view to determine whether the impulse was proportional to  $\sin 2\alpha$  when other things remained the same. I therefore cemented a disk of metal (a half-crown) to an ebonite rod carrying a glass index and hung by a torsion-wire of platinum. The glass index travelled over a card divided into degrees; and the wire to which the upper end of the torsion-wire was soldered also carried a pointer, the position of which could, if desired, be read on a divided card. The disk was suspended between two parallel polar faces of iron. The upper index was turned until, on making and breaking the current, the lower index showed no sign of motion. It could thus be placed within a small fraction of a degree, so that  $\alpha$  was either  $90^\circ$  or  $0^\circ$ . The lower card was then adjusted, and the upper index turned so that the lower rested successively at  $5^\circ$ ,  $10^\circ$ ,  $15^\circ$ , &c. up to  $90^\circ$ . The negative impulse on making, and the positive impulse on breaking, the current were observed by the throw of the lower index. These are given in the second and third columns of the following Table. In the fourth column is a series of numbers in the proportion of  $\sin 2\alpha$ , the largest number being made to agree with the observed positive throw. The close agreement of the other numbers shows clearly that, on breaking the circuit, the impulse is truly proportional to  $\sin 2\alpha$ . Examination shows that the negative impulses, though in reality equal to the others, are apparently much less in amount, that they are not even in proportion, and not only this, but that the corresponding values on either side of  $45^\circ$  are

TABLE I.

Position of rest.	Negative throw.	Positive throw.	Calculated positive throw.
5	1	4.5	4.6
10	2	9	9.1
15	3	13	13.2
20	4.5	17	17.1
25	5	20	20.3
30	6	22.5	23
35	7	24.5	25
40	7.8	26.2	26.2
45	8.8	26.5	26.5
50	8.5	26.2	26.2
55	8.2	24.5	25
60	7.8	22	23
65	7.5	20	20.3
70	6.5	16	17.1
75	5.5	12.5	13.2
80	3.5	9	9.1
85	2	4	4.6

not the same. This want of symmetry is clearly shown by fig. 1. The discrepancy is due to the fact that the disk is brought to rest by the damping action of the field as well as by the torsion of the wire, and that the damping action is greater as the angle is less, being  $\propto \cos^2 \alpha$ .

Fig. 1.



I thought it would be interesting to determine to what angle the disk would be thrown if the torsion of the wire did not act. I therefore suspended, instead of the disk, the coil used in the absolute experiments by a silk thread, adjusted the lower card by the method of no throw, and brought the index to rest successively over  $10^\circ$ ,  $20^\circ$ ,  $30^\circ$ , &c. up to  $90^\circ$ . The index came to rest at the series of positions shown in column 2 of the following Table:—

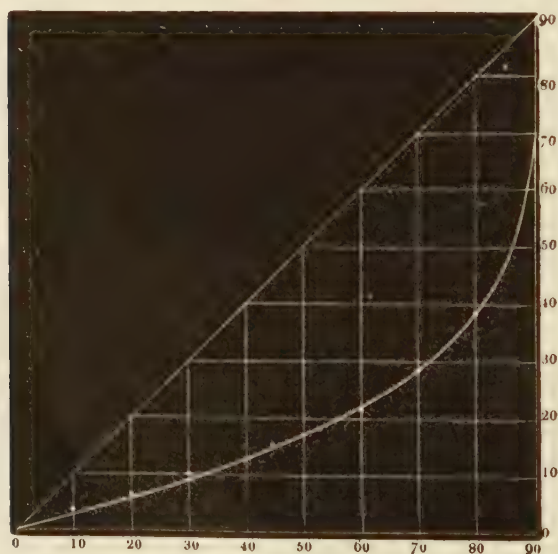


TABLE II.

Pointer fell	
From	To
10	3.6
20	6
30	10
40	13
45	16
50	18
60	22
70	29
80	39

The same results are shown graphically in fig. 2. It is interesting to note that the curve shown is a natural curve depending on circular functions only. It is independent of the nature of material, such as conductivity, moment of inertia, or of the strength to which the field is made to grow from

Fig. 2.



zero. It is subject to a small error, for I did not destroy the residual magnetism. That the effect of this is appreciable is evident, for in one series of experiments with a disk the throw on making was always from  $45^\circ$  to  $33^\circ$ ; but the first time that the direction of the magnetizing current was changed the throw was from  $45^\circ$  to  $35^\circ$ , after which it was from  $45^\circ$  to  $33^\circ$ , as before. This diminution at the first reversal was always the same. I found almost the same fall with the half-crown as with the coil, and with one cell as with ten cells. There were slight differences, but not more than draughts from which I did not shield the needle would have accounted for. The lower angle can be read with precision, but the higher angles become difficult to observe as the damping influence diminishes. The position  $\alpha = 90^\circ$  is one of instability; for however slight a velocity is given to the disk, it will not be brought to rest for a considerable time, owing to the very minute nature of the squares of the cosines of angles nearly equal to  $90^\circ$ .

The last series of experiments was made with a view to determine whether the strength of field determined by observation of the throw of the disk at breaking agreed with the strength determined by some recognized method. I therefore made a small coil of twelve turns of copper wire of 1.45 centim. radius and with a resistance of 0.085 ohm. The area of the coil was 79.4 square centim. The moment of inertia of coil and index was found by comparison with a cylinder to be 58.1 units, and the torsional value of the supporting wire to be 17,000 units. The plane of the coil was adjusted by the usual method to zero, and then set to  $45^\circ$ . The currents from 10, 9, 8, &c. to 1 Grove cells were sent in succession through the coils of the electromagnet and through a Siemens electro-dynamometer. The following Table shows the amounts of the positive and negative impulses, the strengths of the magnetizing currents in amperes, and the field-intensities calculated from the positive throws by the formula

$$H^2 = 9311000 \times \text{Throw measured in degrees.}$$

TABLE III.

Number of cells.	Magnetizing current, in amperes.	Negative throw.	Positive throw.	Calculated field, in absolute units.
10	11.85	10.5	27.5	16,000
9	11.2	9	26	15,600
8	10.44	8.2	24.5	15,100
7	9.47	7	22.5	14,500
6	8.63	6	21.3	14,100
5	7.60	4.8	19.2	13,400
4	6.53	3.3	16.5	12,400
3	5.18	2.2	13	11,000
2	3.67	1	8	8,630
1	1.83	0.2	2.8	5,070

The ends of the coil which were soldered together were then unsoldered without disturbing the soldered connexion between the torsion-wire and one end. The other end was bent so as to dip into a small mercury-cup in the axial line, so that a known current, measured by a second electro-dynamometer, could be sent through the coil. During this change no part of the apparatus was moved at all ; it was, however, necessary to redetermine the zero position, which was now rather more difficult, for the resistance of the torsion-wire was so great in comparison with that of the coil alone, that the throw at any angle was only about one tenth of what it was before. As before, the current from 10 to 1 cells was sent successively through the coils of the electromagnet and an electro-dynamometer. The current from a Daniell cell was sent through the suspended coil and measured. In the fourth column of the following Table will be found the deflection of the coil due to currents tabulated in columns 2 and 3. In the fifth column is the deflection due to the residual magnetism; and in the sixth column the strength of field in absolute units, calculated from the formula

$$H = \frac{3.73 \times \text{deflection in degrees}}{\text{deflecting current in absolute units} \times \cos \delta}$$

TABLE IV.

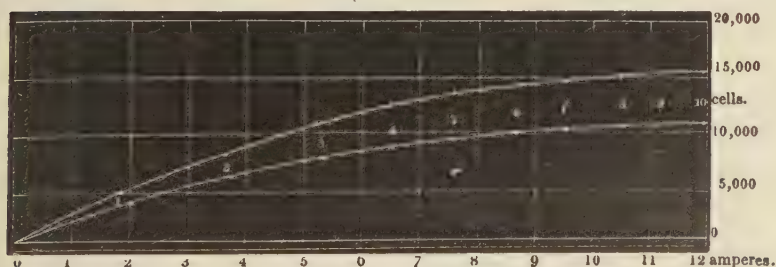
Number of cells.	Magnetizing current, in amperes.	Deflecting current, in amperes.	Deflection = $\delta$ .	Deflection due to residual magnetism.	Calculated field, in absolute units.
10	11.92	.514	65	4	11,200
9	11.05	.530*	64	4	10,260
8	10.52	.502	63	4	10,320
7	9.48	.496	62.5	4	10,150
6	8.63	.480	61.5	4	10,050
5	7.60	.480	60.3	4	9,470
4	6.45	.480	59	4	8,930
3	5.14	.480	57	4	8,120
2	3.67	.480	51.5	4	6,470
1	1.98	.480	40.5	4.5	4,140

\* Obviously over-estimated, hence small results.

The residual magnetism was always the same till one cell only had been employed to excite the electromagnet, when the deflection was clearly greater. This I repeated several times with one and with more than one cell: a deflection of  $4\frac{1}{2}^\circ$  was always obtained from one cell, and of  $4^\circ$  from more than one cell. To obtain a still higher residual magnetic effect, I drew the terminal along a fine wire and gradually diminished the field; by this means I obtained a residual field giving a deflection of  $5^\circ.4$ . The magnetic fields corresponding to the deflections 4,  $4\frac{1}{2}$ , and  $5.4$  are 312, 352, and 422 absolute units.

Fig. 3 shows the field-intensity measured by the two

Fig. 3.





methods. They do not agree, nor are they quite proportional, nevertheless they are of the same order of magnitude. The discrepancy is greater than would be expected from errors of an experimental kind, even though the apparatus was hastily improvised. Nevertheless the agreement, such as it is, shows that it will be worth while to carry out a series of experiments with the accuracy and care that are needed in physical investigations. This I intend to do as soon as I am able. It will then perhaps be possible to tell whether this method of determining conductivity or field-intensity is to be relied upon: it certainly in convenience and simplicity compares very favourably with any of the usual methods.

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XX. *Experiments on the Velocity of Sound in Air.*

By D. J. BLAIKLEY\*.

[Plate XII.]

I HAVE to bring before you this afternoon the results of a few experiments carried out in continuation of the series brought to your notice last November. Before considering the velocities obtained, however, it may be well to show by experiment the reason for the doubt in my mind as to the absolute reliability to be placed upon records obtained from membranes as used by Regnault and Le Roux; and also to explain a little more fully my reason for discarding the use of organ-pipes, speaking under a considerable pressure and with good musical tone, as used by Dulong.

If we take a short tube, say 5 inches long, with a short inner sliding-piece for adjustment of length, and close one end with a diaphragm of gold-beater's skin, against which a bead hung by silk falls, we have a very sensitive resonator for the pitch of about 512 v. If this tube were closed by a rigid material instead of by the skin, its length to give the maximum resonance to the 512 v. fork would be about  $6\frac{1}{4}$  inches; but on drawing the slide to make the tube of this length there

\* Read June 14, 1884, in continuation of paper read November 10, 1883 (Proc. Physical Society, vol. v. p. 319).

is no agitation of the bead: the maximum agitation of the bead, at the present tension of the membrane, is found to be when the tube is about 5 inches long. This is its most sensitive position; but when the fork is vibrating strongly the membrane will record its action, although the length of the tube, from mouth to membrane, is somewhat greater, or less, than is necessary for best effect. Applying this to the case of a membrane stretched across a tube along which a single wave is travelling, as in Regnault's experiments, it would appear that the last possible record of the enfeebled wave would be obtained from its point of maximum condensation; but a record of the wave in the early part of its course, when it is strong, would be obtained from a point in the wave far short of its maximum condensation; so that the length measured by means of the membranes, as travelled by the wave, does not necessarily give the length passed over by a given point in the wave in the measured time. The error, small as it would be when distributed over a great length, would become more appreciable as the tube-length became shorter, and it would in every case lead to an underestimation of the velocity.

In Dulong's experiments care was taken to obtain pipes of good tone; but my experiments have convinced me that such a tone is the worst possible for measurement of wave-lengths. A good musical tone is not pure in the acoustical sense, and the presence of the partials constrains the pitch of the prime to some extent. If the form of pipe were such that its proper tones agreed exactly with the harmonic series, there would not be this difficulty of constrained pitch; but as it would have been exceedingly difficult to construct pipes of this character, I determined to introduce a bulb or pear-shaped portion between the speaking-mouth and the cylindrical tube in which the sliding-plug worked (see Plate XII. fig. 1). By this means tubes were obtained having proper tones quite out of the harmonic order, and therefore capable of giving very pure prime tones.

In November last it was stated that the results obtained from the 11.43 millim. tube were not very reliable. The experiments with this tube have been repeated, and a new tube of 88.19 millim. diameter has been introduced, completing a

series of five tubes, ranging in the proportion of 3 to 5, from 11·43 to 88·19 millim. diameter\*. The results of the new experiments are given in the following table :—

TABLE IV.

Velocity of Sound in dry Air, at 0° C., in tubes.

Diameter of tube .....	11·43 millim.	88·19 millim.
	324·533 324·234	330·29 330·46 330·02 329·72 329·99 330·41 330·09 330·06 330·10 330·20
Means .....	324·383	330·134

In Table V. the results of all the experiments are brought together :—

TABLE V.

Radius, in metres.....	$r$	$r_1$	$r_2$	$r_3$	$r_4$
	·005715	·009524	·015874	·026457	·044095
Velocity at 0° C., in } metres .....	$v$	$v_1$	$v_2$	$v_3$	$v_4$
	324·383	326·902	328·784	329·723	330·134
Mean pitch during } observations .....	$n$	$n_1$	$n_2$	$n_3$	$n_4$
	322·96	260·36	260·18	172·48	131·15
$\sqrt{\frac{1}{n}} \cdot \sqrt{\frac{1}{n_1}} \&c. \dots$					
	·05563	·06197	·06200	·07615	·08732

From these data we may obtain a value for  $V$  = velocity in free air, where  $r = \infty$ , using a modification of the formula

$$v = V \left( 1 - \frac{\alpha}{r} \right). \quad . \quad . \quad . \quad . \quad . \quad (1)$$

\* Through a clerical error the diameters of the tubes were previously given as 11·7, 19·5, 32·5, and 54·1 millim., instead of 11·43, 19·05, 31·71, and 52·91.

The formula  $v = V \left(1 - \frac{\alpha}{r}\right)$  gives only a fictitious value for  $v$  when  $r$  is very small; whereas  $v$  should  $= 0$  when  $r = 0$ , and should  $= V$  when  $r = \infty$ .

Put  $F$  for the ratio  $\frac{v}{V}$ , and  $f$  for  $(1 - F) = \frac{V - v}{V}$ . Then, when  $v = 0$ ,

$$F = 0 \text{ and } f = \frac{V}{V} = 1;$$

and when  $v = V$ ,

$$F = 1 \text{ and } f = 0.$$

When  $F = 0$ ,

$$\log \frac{1}{F} = \infty;$$

when  $F = 1$ ,

$$\log \frac{1}{F} = 0.$$

Therefore in (1), where

$$\frac{\alpha}{r} = \left(1 - \frac{v}{V}\right) = (1 - F),$$

make

$$\frac{\alpha}{r} = \log \frac{1}{F} = \log \frac{V}{v} = \log V - \log v,$$

or

$$r \left( \log \frac{V}{v} \right) = r_1 \left( \log \frac{V}{v_1} \right). \quad . \quad . \quad . \quad . \quad . \quad (2)$$

In (1)

$$\alpha = \sqrt{\frac{\mu}{2np}}$$

(Lord Rayleigh, 'Theory of Sound,' § 347),

$$= \sqrt{\frac{\mu}{2p}} \cdot \sqrt{\frac{1}{n}},$$

so that

$$\left( \alpha - \sqrt{\frac{\mu}{2p}} \right) \propto \sqrt{\frac{1}{n}}.$$

As a slight deviation from accuracy in the relative values of  $\sqrt{\frac{1}{n}}$  would affect the calculated values of  $V$  only to an exceedingly small extent, we may put

$$\sqrt{\frac{1}{n}} = .9, \quad \sqrt{\frac{1}{n_1}} = 1, \quad \sqrt{\frac{1}{n_2}} = 1, \quad \sqrt{\frac{1}{n_3}} = 1.2,$$

$$\text{and } \sqrt{\frac{1}{n_4}} = 1.4$$



in place of the values given in Table V.; and introducing these values into formulæ (1) and (2), we get

$$\frac{1.4}{r_4} = \log \frac{V}{v_4}; \quad \frac{1.2}{\frac{3}{5}r_4} = \log \frac{V}{v_3}, \text{ \&c., \&c.,}$$

or

$$\log V = \frac{10 \log v_4 - 7 \log v_3}{3} \dots \dots \dots (3)$$

From which

$$V = 331.089.$$

In the same way values for  $V$  can be found from any two values of  $v$ —as  $v$  and  $v_1$ ,  $v$  and  $v_4$ , &c., as follows:—

TABLE VI.

V as obtained from	{	$v_4$ and $v_3 = 331.089$
		$v_3$ „ $v_2 = 332.150$
		$v_2$ „ $v_1 = 331.620$
		$v_1$ „ $v = 331.999$
		$v_4$ „ $v_2 = 331.508$
		$v_3$ „ $v_1 = 331.881$
		$v_2$ „ $v = 331.746$
		$v_4$ „ $v_1 = 331.540$
		$v_3$ „ $v = 331.620$
		$v_4$ „ $v = 331.603$

$$\text{Mean } \dots = 331.676$$

As  $v_1$  and  $v_2$  have practically the same values for  $n$ ,  $V$  as obtained from this pair of velocities is uninfluenced by the factor  $\sqrt{\frac{1}{n}}$ ; and if the influence of  $n$  is properly represented by  $\sqrt{\frac{1}{n}}$ , the mean of all the values of  $V$  should agree with  $V$  as obtained from  $v_1$  and  $v_2$ . The mean is 331.676 metres; and the latter value is 331.620, with which the mean is in very close agreement. The pairs of adjacent values  $v_4$  and  $v_3$  &c. are rather ill-conditioned for the determination of  $V$ : the best value of  $V$  should be from the extreme values of  $v$ —that is, the pair  $v_4$  and  $v$ . This value is 331.603—very little different from the value 331.620 obtained from  $v_2$  and  $v_1$ , where there is no variation in the value of  $\sqrt{\frac{1}{n}}$ . From these results it would appear that the influence of the vibrational rate of stationary waves in tubes upon the velocity is properly represented by

$\sqrt{\frac{1}{n}}$ ; but as Lord Rayleigh, in the paragraph quoted, refers to Schneebeli's and A. Seebeck's investigations, based upon Kundt's experiments, we may calculate a value for  $V$  upon their determinations. According to these observers, when  $n$  varies, the diminution of velocity is proportional rather to  $\sqrt{\frac{1}{n^3}}$  than to  $\sqrt{\frac{1}{n}}$ . Taking the pair of velocities  $v$  and  $v_4$ , and substituting  $\sqrt{\frac{1}{n^3}}$  for  $\sqrt{\frac{1}{n}}$ , we get  $V = 334.439$ —manifestly too high, and very different from  $331.620$ , the value obtained from the pair  $v_1$  and  $v_2$ .

In the diagram (Plate XII.) and in Table VIII. I have therefore used  $\sqrt{\frac{1}{n}}$ ; but this, or any modification of it such as  $\sqrt[n]{\frac{1}{n^m}}$ , can only be applicable, and then but approximately, within certain limits.

TABLE VII.

TABLE VIII.

Calculated velocity, in metres, at the pitch of 260 vibrations.	Comparison between values of $v, v_1, v_2, v_3, v_4$ , as observed and as calculated, at the pitch of observations, $V$ being taken as 331.676 metres.							
	Radius.		Velocity, in metres.			Differences.		$n$ , or pitch.
				Observed.	Calculated.	—	+	
323.728	$r$	.005715	$v$	324.383	324.514	...	.131	322.96
326.884	$r_1$	.009524	$v_1$	326.902	326.884	.018	...	260.36
328.792	$r_2$	.015874	$v_2$	328.784	328.792	...	.008	260.18
329.943	$r_3$	.026457	$v_3$	329.723	329.545	.178	...	172.48
330.635	$r_4$	.044095	$v_4$	330.134	330.209	...	.075	131.15

In the diagram (Plate XII.) the curve given by the figures in Table VII. is laid down, and also the observed and calculated values given in Table VIII. To these are added curves for 130, 520, and 1040 vibrations.

In addition to the experiments of which the details are given, many trials were made in the course of adjusting the apparatus. Some of these trials were at pitches other than those finally adopted; and although such results were of no value for exact comparison, the general bearing of them was quite in agreement with the results tabulated. One of these

preliminary trials was a set of five observations with the tube of 52·91 millim. diameter ( $r_3$ ) at the pitch of 260. The mean result was a velocity of 330·27, in place of 329·94 as on Table VII. This trial was made with the tube before the introduction of the bulb-mouth; and the third partial tone was perceptible to the ear, so that the prime may have been influenced a little thereby.

The notes were all purposely kept very weak, so that the excess of pressure in the tubes when sounding, above the barometric pressure, must have been very small indeed. In one of the large tubes ( $r_3$ ) a water-pressure gauge was introduced; but the pressure was barely measurable, certainly not exceeding  $\frac{1}{50}$  inch of water. In the calculations I have therefore assumed that the influence of intensity might be neglected.

The chief conclusions to which these experiments appear to lead are the following:—

1st. The tubes used for the measurement of wave-length, as determined by the length between nodes, must speak with a pure tone; or

2nd. If partials are present, the tubes must be of such form as to have their proper tones in exact agreement with the harmonic series. (Neither of these conditions is easily attainable with ordinary organ-pipes.)

3rd. The air-blast must not constrain the pipe to speak any other pitch than its natural pitch of resonance.

4th. In smooth tubes the diminution of velocity is proportional to  $r^{-1}$  and to  $n^{-\frac{1}{2}}$ , as determined by Helmholtz.

5th. The velocity  $V$  in free air for sound-waves of low intensity, or just audible, is 331·676 metres at 0° C.

6th. The ratio between the two specific heats of air, as deduced from the Newtonian velocity 279·955 metres, and  $V$  as above 331·676 metres, is 1·4036.

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As there is perhaps room for some doubt about the influence of  $n$  being properly represented by  $n^{-\frac{1}{2}}$ , I have not attempted to employ Kirchhoff's equation in place of Helmholtz's; but in abler hands than mine, the experimental results may perhaps be of some assistance in determining one or more of the points involved in these formulæ.

XXI. *On the Alterations in the Electrical Resistances of Metallic Wires, produced by Coiling and Uncoiling.* By JAMES HOPPS, *Superintendent of Workshops, Royal Indian Engineering College, Cooper's Hill\**.

[Plate XIII.]

DURING the past winter, while assisting a pupil to make some resistance-coils, I was struck with the great difference that often existed between the resistance of the wire before it was coiled on to its bobbin and after ; the difference was not always constant or proportional to the length of the wires used, and appeared to be largely influenced by the tension with which the wires were coiled on to the bobbins.

Some of the coils altered so much after winding as to lead to the supposition of their being short-circuited; and on uncoiling several of these and recoiling at a lower tension, the resistance would alter considerably.

The diameter of the bobbin used also appeared to have great influence in producing changes in the resistance.

A great portion of the alterations appeared to be temporary.

As has been observed above, the differences were not always constant ; neither were they regular in their signs, *i. e.* they would sometimes show an increase and sometimes a decrease of resistance, but generally the change would be one of increase.

Having resolved to make some efforts to clear up this matter, I first sought to find what had been done by others in this direction. A very careful search through books and also of the Transactions of the Royal Society afforded no evidence that this field had been even entered upon, *i. e.* any attempt by experiment or otherwise to determine and account for the effects of coiling and uncoiling on the electrical resistance of metallic wires.

After experimenting some weeks, I purposely attended the meeting of this Society on February 23rd to hear a paper, "On the Adjustment of Resistance-Coils," by Prof. Silvanus P. Thompson ; and although some of the difficulties in the way of adjusting resistance-coils were spoken of, yet the difficulty

\* Read June 28th, 1884.



that had given us so much trouble was not once alluded to, either in the paper or in the discussion which followed. At the close of the proceedings, in the course of a short conversation with Prof. Thompson, and in reply to a question from myself, he stated that he had observed that the resistance of a wire was altered by being coiled. Mr. Latimer Clark also observed that he had noticed the change, but added that the changes were not always constant, giving sometimes an increase and sometimes a decrease in the resistance. Now experiments had given me the same results, and had the subject cropped up during the discussion, I had prepared a few notes to give to the meeting.

The fact of having obtained sometimes + and sometimes — readings had puzzled me much, but after the conversation above alluded to I resolved to continue my experiments; and although these are yet far from complete, I have felt it my duty to lay the results already obtained before the Society.

Before going into a description of the apparatus and method employed (part of the apparatus is before you), I would crave a few moments to allude to some of my earlier experiments. These were conducted in a very primitive way; but the results obtained, although appearing so erratic and contradictory, have been in a great measure confirmed by using the more elaborate method employed later on. In confirmation of this I would draw your attention to the great resemblance which exists between the two curves on the diagram, which are the curves of copper wires produced by hand- and machine-winding respectively.

The method first employed to investigate this effect was to let the wire under test form one side of a Wheatstone bridge, doubling the wire into a loop as in a resistance-coil, and rolling it by hand on to a cylinder or other shapes in wood. The resistance could thus be taken after each operation without the necessity of altering the connexions.

The time lost in waiting until the heat imparted to the wire through handling had disappeared was great, and the uncertainty as to the tension with which the wire was coiled and uncoiled caused me to seek some other method.

After many schemes the one before you was adopted. Bearing in mind that many of the wires to be experimented upon

would not be insulated, and would be of many different diameters and rigidities, it was very early evident that the drum on which the wires were to be coiled would also have to insulate each convolution from its neighbour as well as to wind up the wire. The different diameters and rigidities also determined the necessity of being able to vary the tension. The insulation is obtained by using an ebonite drum to receive the wire ; on this drum a right- and left-handed screw has been cut. The variation in the tension may be obtained in two different ways, or by a combination of both:—1st, by altering the load carried in the little waggon which runs up and down the inclined plane ; 2nd, by altering the angle of inclination of the plane ; or we may combine both if necessary.

As the application of longitudinal strain to a wire while being tested for resistance has been shown to be considerable, it was necessary to relieve the wire from the strain due to the load before taking the resistance, otherwise the changes due to strain would have been included in the readings. To remove the strain, the waggon on arriving at the bottom of the plane rests against a stop ; on being drawn to the top the plane is brought to a position slightly above the horizontal ; these allowing in both cases the drum to slightly unwind itself, and consequently the strain on the wire is almost entirely removed.

The ebonite drum, as before observed, has a right- and left-handed screw cut upon it ; these meet in the middle of its length. A screw holding down an ebonite cap here passes through the inside of the loop of the wire under test, and fixes it firmly, but without injury, to the drum ; the ends of the wire are carried up the plane to two binding-screws, and with the necessary leading wires form one side of a Wheatstone bridge.

A long length of stout whipcord is attached to the middle of a winding drum underneath the head of the plane, and the ends, after being coiled between the empty threads of the ebonite drum (starting from the centre), are fixed to the ends of the drum. On turning the drum below, the cords pull on the top part of the ebonite drum, causing it to revolve ; and at the same time that the cord is being payed off, the wire under test is being coiled on in its place. This is continued until the waggon arrives at the top ; a pawl working on a ratchet-

wheel prevents the waggon running back until the plane has been brought to a horizontal position, where, after resting five minutes, the resistance is taken. The operations are now reversed; and after a similar rest at the bottom, the resistance is again taken. And these operations are repeated, each operation taking about six minutes, giving an average of ten per hour; they were generally continued for three hours, giving for each series about thirty readings, and then allowed to stand until the following evening, all strain being previously removed.

The temperature of the laboratory was carefully regulated each evening, for two hours before commencing work, to the same temperature as on the previous evening, and kept constant within half a degree Fahr.  $\pm$ .

In the case of some wires as many as 380 readings have been taken altogether; this was on lead wire No. 5. At the end of the seventh series the wire broke.

The curves of resistance of four of the seven series of tests on this wire is very interesting. It will be observed that, while being very similar to each other, there is a point marked (*a*) on each series where coiling and uncoiling produce an increase in the resistance. Again, the wonderful power of recovery which is shown by the wire after each rest is very marked; the normal condition would appear to be to give positive and negative readings, and that this condition is upset after a time. The inability to recover this condition has suggested that, when this point has been arrived at, it might be said to represent the commencement of a kind of electrical fatigue.

There are some other points on this diagram, and which are more or less repeated by every other wire that I have tested, which furnish matter for speculation; such as—why should coiling generally produce a less effect than uncoiling? and why should the signs be generally different? and why should those signs in many cases become reversed?

An *increase* of resistance on uncoiling and a *decrease* on coiling take place with lead, copper, German silver, aluminium, and magnesium; and also with the first few operations on soft iron wire, after which the signs are completely changed.

An increase almost invariably follows coiling and uncoiling with zinc, but the effect of coiling varies from one half to one thirtieth of the effect of uncoiling.

The difference between coiling and uncoiling, or, we might say, the amplitude of the differences of resistances, is greatest in the case of magnesium and least in the case of aluminium; the latter, on referring to the curves, will be seen to alter very little indeed.

The amplitude of the differences in the case of hard-drawn German silver is not so great after a few series; and when annealed, after showing great increases after standing at rest, the final series approach very near to that of the hard-drawn wire, which is strong evidence indeed that the wire has become harder through repeated coiling and uncoiling.

The length of the wires were very carefully taken before and after the experiments, and the necessary calculations made for alterations in length and cross-section according to the formula  $R \propto \frac{l}{a}$ , in which  $R$  = the resistance,  $l$  = the length, and  $a$  = the area of the cross section.

After making these corrections, the changes in the resistance remaining unaccounted for are:—

Metals.	Of the increase on the original resistance.	Of the actual observed change.
Iron .....	2·3 per cent.	81·64 per cent.
Lead (average of six) .....	1·27 „	2·91 „
Copper .....	1·18 to 1·42 per cent.	57·58 to 60·7 per cent.
Zinc .....	1·23 to 2·16 „	23·6 to 42·4 „
Aluminium .....	0·77 to 2·206 „	41·15 to 72·01 „
German silver (annealed) ...	0·054 to 0·171 „	11·89 to 21·6 „
Magnesium No. 2.....	1·549 per cent.	

With magnesium No. 2, from a different sample from No. 1, the wire became shorter; and the resistance, which should have fallen ·0745 per cent., actually increased 1·475 per cent., being equivalent to a difference of 1·549 per cent. on the original resistance unaccounted for.

With magnesium No. 1 the actual increase of resistance amounted to 2·16 per cent. on the original resistance, whereas theoretically it should have increased 3·39 per cent., or 1·23 per cent. greater than really took place; or we may say that



of the theoretical increase only 54·35 per cent. was visible, showing that the specific conductivity of the wire had risen. Four portions of this wire were tested, and the results were all very near alike.

On examining the results obtained with German silver No. 5 (annealed), which after all is most likely to interest us, owing to its employment in resistance-coils, we find that the total increase was equal to ·454 per cent.; and after deducting ·4 per cent., which is due to increase in length and diminution of section, there still remains unaccounted for ·054 per cent. on the original resistance, or 11·89 per cent. of the whole observed change.

With German silver (hard-drawn) the results are very curious. Here the length actually decreased; and on making the necessary corrections, the resistance should have shown a decrease of ·284 per cent.; but the actual decrease was only equal to ·036 per cent., not low enough by ·248 per cent.; or we may say that of the theoretical decrease only 12·26 per cent. was visible.

On examining the curves from the iron wires Nos. 3 and 4, it will be observed that at the commencement uncoiling produced a very large *increase*, while coiling produced a small *decrease*; but after sixteen operations in one case and twenty-one in the other, the signs became reversed, and this continued throughout the remaining series of the two wires.

On page 74, vol. vi. of the 'Proceedings of the Physical Society,' I find a paper by Mr. Herbert Tomlinson, in which he says that "the behaviour of nickel is especially worthy of notice, because in it longitudinal traction, when not carried beyond a certain limit, *diminishes* the electrical resistance in spite of the increase of length and diminution of section which ensues."

I have not been able to obtain wires in nickel, but, according to the results obtained, some samples of magnesium appear to have the same property.

At the last moment Prof. Stocker has shown me that in *Die Electricität*, by Wiedemann, it is noted that "the coiling of a copper or iron wire increases, whilst the uncoiling diminishes the specific resistance about 0·003 of the total value of the same."

And, again, in *Die Physik*, vol. iii., by Mousson, that "the coiling of a wire upon a cylinder slightly increases the resistance, in consequence, as is supposed, of tension; uncoiling diminishes it again. Under similar circumstances, the changes amounted to 0·0032 in the case of copper and to 0·0056 in iron, of their total resistances."

It will be observed that both these descriptions are contrary to what I must conclude from my own experiments.

Having made some inquiries from a friend of mine who had charge of the testing department in the cable factory of J. B. Pirelli, F. Casassa et C<sup>ie</sup>, of Milan, he has supplied me with data which show that the specific conductivity of the copper conductors have fallen in many cases  $1\frac{1}{2}$  per cent. during manufacture, and when encased in lead tubes they have often fallen over 2 per cent. In all cases the necessary corrections have been made for increase of length and diminution of section due to strain in passing through the covering machines. Possibly the greater loss in the lead-encased core may be due to a damping-effect from the lead, but the bulk of the increase of resistance must be due to some other cause. These cables were manufactured under very strictly enforced conditions for the Italian State Telegraph-stores; and the tests taken by government officials, ten weeks after they had been sent from the factory, were in all cases within 0·2 per cent. of the final tests in the factory, showing conclusively that the changes were in a great measure permanent.

I have therefore come to a very decided conclusion that the changes in the resistance are not altogether the result of changes in form, and that their cause must be sought for elsewhere.

Many theories have suggested themselves, but none are entirely satisfactory.

One theory was that, in coiling, the decrease of resistance was due to a thickening of the wire on its internal side and a thinning of the external side, thus bringing the centre of area inwards, and so making the actual distance the current would have to travel shorter, which would be equivalent to making the wire shorter; and then on uncoiling, the displacement of the molecules, due to slipping on each other when seeking to regain their original position, would have the effect of increasing their distance apart, and consequently increasing the

resistance. But the weak point in this theory is that it will not account for the change of signs which so often takes place, nor will it account for the zinc wires giving increased resistances on coiling.

Another theory, which appears more promising, was that, while being coiled and uncoiled, the wires were subject to strains of a torsional kind, which might be due to their having a certain amount of residual twist in them, owing to the way in which they have been coiled on to the drums on the bench of the wire drawer; and that on being coiled and uncoiled on their bobbins this twist might be increased or decreased, so giving different amounts in the resistance. But from experiments I have made, which seem to me quite conclusive, it appears that although there is a certain amount of twisting and untwisting produced by being wound on to the bobbins, yet this fails to account for the residue of the observed changes.

With reference to the effects on the permanency of value of a set of resistance-coils which are only subjected to one winding, I have not yet sufficient data to lay before you; but, so far as I have gone into this part of the subject, I believe that the immediate alterations on coiling the wires on the bobbins are to a great extent affected by the tension and the speed with which they are wound, the thickness and kind of insulator employed (cotton-covered wires appear to be less affected than silk-covered wires), and also by the diameter of the bobbins on which the wire is wound (the smaller the bobbin the greater the alteration). But further experiments are necessary to put these beyond doubt.

Appended to this paper are a few tables showing the actual readings in the first series of several of the wires tested (these readings include the resistance of the leading wires, .0274). These, together with the curves (Pl. XIII.), may be of some service in assisting to a conclusion as to the probable cause of the changes in the resistance of wires produced by coiling and uncoiling.

*Actual Readings and Differences produced by Coiling and Uncoiling of Lead Wire No. 5 (first four series only).*

U represents uncoiled ; C represents coiled.

	1st Series.		2nd Series.		3rd Series.		4th Series.	
	Resist- ance.	Differ- ence.	Resist- ance.	Differ- ence.	Resist- ance.	Differ- ence.	Resist- ance.	Differ- ence.
U .....	·2923		·3087		·3198		·3340	
C .....	22	+·0001	88	+·0001	·3196	-·0002	39	-·0001
U .....	33	+·0011		+·0015		+·0017	56	+·0017
C .....	32	-·0001	·3103	+·0001	·3213	-·0002	52	-·0004
U .....	39	+·0007	04	+·0008	11	+·0017	64	+·0012
C .....	40	+·0001	12	+·0008	28	-·0002	60	-·0004
U .....	45	+·0005	20	+·0008	26	+·0011	72	+·0012
C .....	47	+·0002	28	+·0001	37	-·0002	68	-·0004
U .....	52	+·0005	28	.....	35	+·0007	78	+·0010
C .....	54	+·0002	36	+·0008	42	.....	77	-·0001
U .....	59	+·0005	37	+·0001	42	+·0007	86	+·0009
C .....	61	+·0002	43	+·0006	49	.....	85	-·0001
U .....	67	+·0006	44	+·0005	49	+·0008	93	+·0008
C .....	69	+·0002	49	+·0002	57	.....	93	.....
U .....	73	+·0004	51	+·0006	57	+·0007	3400	+·0007
C .....	77	+·0004	57	+·0001	64	.....	00	.....
U .....	81	+·0004	58	+·0005	64	+·0008	5	+·0005
C .....	84	+·0003	63	+·0001	72	+·0001	7	+·0002
U .....	88	+·0004	64	+·0005	73	+·0005	14	+·0007
C .....	91	+·0003	69	+·0002	78	+·0001	16	+·0002
U .....	94	+·0003	71	+·0006	79	+·0007	20	+·0004
C .....	98	+·0004	77	+·0003	86	+·0001	22	+·0002
U .....	·3001	+·0003	80	+·0005	87	+·0006	26	+·0004
C .....	4	+·0003	85	+·0002	93	+·0001	28	+·0002
U .....	7	+·0003	87	+·0005	94	+·0005	32	+·0004
C .....	10	+·0003	92	+·0002	99	+·0001	36	+·0004
U .....	14	+·0004	94	+·0004	·3300	+·0005	39	+·0003
C .....	17	+·0003	98		5	+·0001	41	+·0002
U .....	20	+·0003	Rested here 21 hours ; no change on resuming.		6	+·0006	43	+·0002
C .....	24	+·0004			12	+·0002	46	+·0003
U .....	28	+·0004			14	+·0005	49	+·0003
C .....	30	+·0002			19	+·0001	53	+·0004
U .....	34	+·0004			20	+·0005	56	+·0003
C .....	38	+·0004			25	+·0002	59	+·0003
U .....	40	+·0002			27	+·0006	59	+·0003
C .....	42	+·0002			33	+·0003	62	+·0003
U .....	45	+·0003			36	+·0004	65	+·0003
C .....	47	+·0002			40		68	+·0003
U .....	51	+·0004	Rested here 22 hours ; no change on resuming.				71	+·0003
C .....	56	+·0005					75	+·0004
U .....	59	+·0003					79	+·0004
C .....	62	+·0003					82	+·0003
U .....	66	+·0004					85	+·0002
C .....	69	+·0003					87	+·0003
U .....	66	+·0003					90	+·0003
C .....	70	+·0004					93	+·0003
U .....	76	+·0006					96	+·0003
C .....	79	+·0003					99	+·0003
U .....	83	+·0004	Loss after standing 21 hours=·0003.				·3502	+·0003
C .....	87	+·0004					5	+·0003
U .....	90	+·0003					8	+·0001
C .....	90	.....					9	



# Aluminium Wire.

No. 1.				
	1st Series.		2nd Series.	
	Resistance.	Difference.	Resistance.	Difference.
U ...	·08004	.....	·08042	— ·00005
C ...	4	+ ·00018	37	+ ·00011
U ...	22	— ·00007	48	— ·00006
C ...	15	+ ·00011	42	+ ·00007
U ...	26	— ·00008	49	— ·00006
U ...	18	+ ·00010	43	+ ·00010
U ...	28	— ·00006	53	— ·00006
C ...	22	+ ·00010	47	+ ·00011
U ...	32	— ·00007	58	— ·00005
C ...	25	+ ·00009	53	+ ·00008
U ...	34	— ·00007	61	— ·00005
C ...	27	+ ·00010	56	+ ·00008
U ...	37	— ·00011	64	— ·00005
C ...	26	+ ·00009	59	+ ·00008
U ...	35	— ·00005	67	— ·00004
C ...	30	+ ·00008	63	+ ·00006
U ...	38	— ·00005	69	— ·00003
C ...	33	+ ·00008	66	+ ·00005
U ...	41	— ·00006	71	— ·00003
C ...	35	+ ·00009	68	+ ·00004
U ...	44	— ·00005	72	— ·00004
C ...	39	+ ·00007	68	+ ·00005
U ...	46	— ·00004	73	— ·00004
C ...	42	+ ·00006	69	+ ·00005
U ...	48	— ·00004	74	— ·00003
C ...	44	+ ·00005	71	+ ·00005
U ...	49	— ·00003	76	— ·00003
C ...	46	+ ·00006	73	+ ·00004
U ...	52	— ·00004	77	— ·00003
C ...	48	+ ·00007	74	+ ·00004
U ...	55	— ·00003	78	— ·00003
C ...	52	+ ·00008	75	+ ·00004
U ...	60	— ·00004	79	— ·00003
C ...	56	+ ·00005	76	+ ·00005
U ...	61	— ·00003	81	— ·00003
C ...	58	+ ·00003	78	+ ·00005
U ...	61	— ·00002	83	— ·00004
C ...	59	+ ·00003	79	+ ·00003
U ...	62	— ·00002	82	— ·00003
C ...	60	+ ·00003	79	+ ·00003
U ...	63	— ·00002	82	— ·00002
C ...	61	+ ·00002	80	+ ·00002
U ...	63	— ·00001	82	
C ...	62	+ ·00002		
U ...	64	— ·00001		
C ...	63	+ ·00001		
U ...	64	.....		
C ...	64	+ ·00001		
U ...	65	.....		
C ...	65	+ ·00001		
U ...	66			
Rested here 21 hours ; loss by standing ·00023.			Rested here 45 hours ; and gained by standing ·00019.	

## German-silver Wires.

	No. 4 (hard drawn).				No. 5 (annealed).			
	1st Series.		2nd Series.		1st Series.		2nd Series.	
	Resist- ance.	Differ- ence.	Resist- ance.	Differ- ence.	Resist- ance.	Differ- ence.	Resist- ance.	Differ- ence.
U...	1·53483	—·00058	1·53541	—·00096	1·51821	—·00161	1·52150	—·00010
C...	25	+·00037	445	+·00107	982	—·00019	140	+·00010
U...	62	—·00050	552	—·00094	963	+·00018	150	—·00008
C...	12	+·00053	458	+·00087	981	—·00001	142	+·00007
U...	65	—·00052	545	—·00077	980	.....	149	—·00011
C...	13	+·00047	468	+·00088	980	.....	138	+·00012
U...	60	—·00055	556	—·00085	980	+·00012	150	—·00014
C...	05	+·00040	471	+·00059	992	.....	136	+·00006
U...	45	—·00043	530	—·00045	992	—·00004	130	—·00008
C...	02	+·00040	485	+·00039	988	+·00012	122	+·00018
U...	42	—·00039	524	—·00044	1·52000	—·00006	140	—·00017
C...	03	+·00039	480	+·00038	1994	+·00010	123	+·00012
U...	42	—·00037	518	—·00036	2004	—·00004	135	—·00015
C...	05	+·00036	482	+·00034	2000	+·00010	120	+·00012
U...	41	—·00041	516	—·00038	2010	—·00007	132	—·00013
C...	00	+·00040	478	+·00023	2003	+·00017	119	+·00010
U...	40	—·00040	501	—·00029	2020	—·00010	129	—·00018
C...	00	+·00036	472	+·00027	2010	+·00015	111	+·00009
U...	36	—·00036	499	—·00033	2025	—·00011	120	—·00012
C...	00	+·00035	66	+·00019	2014	+·00017	108	+·00006
U...	35	—·00039	85	—·00026	2031	—·00010	114	—·00014
C...	1·53396	+·00038	59	+·00021	2021	+·00017	100	+·00015
U...	434	—·00039	80	—·00028	2038	—·00011	085	—·00012
C...	395	+·00039	52	+·00021	2027	+·00013	073	+·00011
U...	434	—·00040	73	—·00036	2040		062	—·00006
C...	394	+·00029	37	+·00025			068	+·00003
U...	423	—·00033	62	—·00014			071	—·00006
C...	390	+·00031	48	+·00014			065	+·00005
U...	421	—·00031	62	—·00028			070	.....
C...	390	+·00035	34	+·00024			070	+·00001
U...	425	—·00034	58	—·00027			071	—·00001
C...	391	+·00034	31	+·00021			070	+·00002
U...	425		52				070	—·00002
C...							073	+·00003
U...	Rested for 21 hours; gained ·00116.		Rested for 21 hours; gained ·00109.		Rested for 16 hours; gained ·00110.		Rested for 26 hours; gained ·00231.	

### Magnesium Wires.

No. 1. Length at commencement =55·08 inches.				No. 2. Length at commencement =86 inches.			
1st Series.		2nd Series.		1st Series.		2nd Series.	
Resist- ance.	Differ- ence.	Resist- ance.	Differ- ence.	Resist- ance.	Differ- ence.	Resist- ance.	Differ- ence.
U... 29195	-·00135	29488	-·00104	44079	-·00264	44312	-·00164
C... 60	+·00150	384	+·00141	3815	+·00333	148	+·00220
U... 210	-·00135	525	-·00115	4148	-·00215	368	-·00163
C... 75	+·00150	410	+·00145	3933	+·00283	205	+·00199
U... 225	-·00127	555	-·00128	4216	-·00225	404	-·00172
C... 98	+·00157	427	+·00140	3991	+·00254	232	+·00149
U... 255	-·00110	567	-·00122	4245	-·00222	381	-·00158
C... 145	+·00120	445	+·00122	4023	+·00234	223	+·00162
U... 265	-·00110	567	-·00132	257	+·00195	385	-·00154
C... 155	+·00125	435	+·00130	062	+·00210	231	+·00155
U... 280	-·00100	565	-·00100	272	-·00181	386	-·00151
C... 180	+·00123	465	+·00110	091	+·00209	235	+·00145
U... 303	-·00125	575	-·00102	300	-·00174	380	-·00138
C... 178	+·00099	473	+·00112	126	+·00199	242	+·00139
U... 277	-·00091	585	-·00103	325	-·00157	381	-·00140
C... 186	+·00098	482	+·00112	168	+·00062	241	+·00143
U... 284	-·00099	594	-·00106	230	-·00142	384	+·00138
C... 185	+·00107	488	+·00117	088	+·00160	246	+·00135
U... 292	-·00087	605	-·00109	248	-·00167	381	-·00133
C... 205	+·00090	496	+·00114	081	+·00170	242	+·00138
U... 295	-·00090	610	-·00105	251	-·00162	380	-·00139
C... 205	+·00080	505	+·00112	089	+·00161	241	+·00135
U... 285	-·00060	617	-·00112	250	-·00166	376	-·00124
C... 225	+·00102	505	+·00115	084	+·00161	244	+·00129
U... 327	-·00090	620	-·00095	245	-·00160	368	-·00129
C... 237	+·00108	525	+·00100	085	+·00161	239	+·00131
U... 345	-·00095	625	-·00090	246	-·00146	370	-·00129
C... 250	+·00112	535	+·00087	100	+·00149	241	+·00127
U... 362	-·00097	622	-·00077	249	-·00137	368	-·00128
C... 265	+·00102	545	+·00100	112	+·00139	240	+·00114
U... 377	-·00063	645	-·00098	251		354	-·00112
C... 314	+·00120	547	+·00100			242	+·00108
U... 434	-·00079	647	-·00081			350	-·00115
C... 355	+·00083	566	+·00094			235	+·00116
U... 438	-·00072	660	-·00087			351	-·00112
C... 366	+·00079	573	+·00094			239	+·00105
U... 445	-·00060	667				344	-·00106
C... 385	+·00073					238	+·00103
U... 458	-·00068					341	-·00104
C... 390	+·00072					237	+·00105
U... 462	-·00065					342	
C... 397	+·00071						
U... 468							

Rested here 21  
hours; resistance  
rose to 29488;  
showing gain by  
standing of 000

## Iron Wires (soft).

No. 3.					No. 4.				
1st Series.		2nd Series.		1st Series.		2nd Series.			
Resist- ance.	Differ- ence.	Resist- ance.	Differ- ence.	Resist- ance.	Differ- ence.	Resist- ance.	Differ- ence.		
U... 34735	+00007	34995	+00094	34720	+00015	34970	+00090		
O... 42	+00032	35089	-00067	35	+00043	35060	-00045		
U... 74	-00002	022	+00071	78	-00006	15	+00050		
O... 72	+00040	093	-00046	72	+00043	65	-00037		
U... 812	-00004	047	+00054	34815	+00001	28	+00046		
O... 16	+00026	101	-00059	16	+00021	74	-00044		
U... 42	+00005	042	+00045	37	+00005	30	+00038		
O... 47	+00015	097	-00058	42	+00018	68	-00033		
U... 62	+00008	039	+00059	60	+00008	35	+00042		
O... 70	+00016	098	-00050	68	+00012	77	-00045		
U... 86	+00016	048	+00056	80	+00018	32	+00038		
O... 902	+00012	104	-00046	98	+00022	70	-00039		
U... 14	+00018	058	+00049	34920	+00010	31	+00048		
O... 32	-00004	107	-00050	30	.....	79	-00037		
U... 28	+00028	057	+00058	30	+00010	42	+00046		
O... 56	-00036	115	-00059	40	-00010	88	-00043		
U... 20	+00052	056	+00061	30	+00023	45	+00054		
O... 72	-00020	117	-00055	53	-00023	99	-00030		
U... 52	+00040	062	+00062	30	+00038	69	+00050		
O... 92	-00028	124	-00066	68	-00028	35119	-00034		
U... 64	+00051	058	+00060	40	+00024	085	+00043		
O... 35015	-00033	118	-00042	64	-00019	128	-00016		
U... 4982	+00059	076	+00038	45	+00020	112	+00033		
O... 5041	-00039	114	-00030	65	-00015	45	-00021		
U... 5002	+00056	084	+00034	40	+00035	24	+00035		
O... 58	-00039	118	-00016	75	-00025	59	-00015		
U... 19	+00060	102	+00040	50	+00048	44	+00036		
O... 79	-00041	142	-00021	98	-00030	80	-00010		
U... 38	+00058	121	+00043	68	+00046	70	+00029		
O... 96	-00041	164	-00019	35014	-00026	99	-00009		
U... 55		145	+00047	34988	+00062	90	+00036		
O... 32		192	-00016	35050	-00028	35226	-00007		
U... 32		176		32	+00056	19	+00049		
C... 88				88	-00023	68	-00012		
U... 65				65		56			
C... 65									
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## Copper Wire.

	No. 4.			
	1st Series.		2nd Series.	
	Resistance.	Difference.	Resistance.	Difference.
U .....	·17762	—·00003	·17882	—·00002
O .....	59	+·00019	·17880	+·00023
U .....	78	—·00003	·17903	—·00009
C .....	75	+·00013	·17894	+·00020
U .....	88	—·00003	·17914	—·00010
C .....	85	+·00012	04	+·00024
U .....	97	—·00003	28	—·00008
O .....	94	+·00014	20	+·00016
U .....	·17808	—·00004	36	—·00006
C .....	04	+·00021	30	+·00011
U .....	25	—·00005	41	—·00007
O .....	20	+·00011	34	+·00014
U .....	31	—·00004	48	—·00005
C .....	27	+·00012	43	+·00017
U .....	39	—·00005	60	—·00008
O .....	34	+·00009	52	+·00015
U .....	43	—·00005	67	—·00008
C .....	38	+·00009	59	+·00014
U .....	47	—·00004	73	—·00008
O .....	43	+·00011	65	+·00013
U .....	54	—·00005	78	—·00007
C .....	49	+·00011	71	+·00013
U .....	60	—·00005	84	—·00007
O .....	55	+·00009	77	+·00012
U .....	64	—·00005	89	—·00007
O .....	59	+·00007	82	+·00011
U .....	66	—·00003	93	—·00006
O .....	63	+·00008	87	+·00010
U .....	71	—·00004	97	—·00006
O .....	67	+·00007	91	+·00007
U .....	74	—·00004	98	—·00007
C .....	70	+·00007	91	+·00008
U .....	77	—·00003	99	—·00003
O .....	74	+·00006	96	+·00009
U .....	·17880		·18005	
Rested here 21 hours ; gained by standing ·00002.			Rested here 21 hours ; loss by standing ·00039.	

## Zinc Wires.

	No. 5.		No. 6.	
	Resistance.	Difference.	Resistance.	Difference.
U .....	14063	+·00014	14038	+·00027
C .....	077	+·00018	065	+·00025
U .....	095	+·00009	090	+·00003
C .....	104	+·00024	087	+·00032
U .....	128	+·00007	119	+·00002
C .....	135	+·00011	117	+·00021
U .....	146	+·00003	138	.....
C .....	149	+·00011	138	+·00014
U .....	160	+·00004	152	+·00003
C .....	164	+·00009	149	+·00015
U .....	173	+·00005	164	+·00001
C .....	178	+·00008	163	+·00015
U .....	186	+·00004	178	+·00002
C .....	190	+·00010	180	+·00011
U .....	200	+·00005	191	+·00002
C .....	205	+·00007	193	+·00012
U .....	212	+·00007	205	+·00003
C .....	219	+·00008	208	+·00010
U .....	227	+·00012	218	+·00003
C .....	239	+·00005	221	+·00009
U .....	244	+·00013	230	+·00005
C .....	257	+·00004	235	+·00010
U .....	261	+·00009	245	+·00006
C .....	270	+·00002	251	+·00019
U .....	272	+·00006	270	+·00018
C .....	278	.....	288	
U .....	278	+·00017		
C .....	295			
	Wire broke.		Wire broke.	

XXII. *On some Thermal and Volume Changes attending Mixture.* By FREDERICK GUTHRIE\*

[The paragraphs are numbered in sequence with those of my previous communications on Salt-Solutions and Attached Water.]

§ 256. It may be taken as a rule that solid crystalloids are more soluble in liquids when the two are at a higher than when at a lower temperature. The apparent exceptions to this rule are all, I believe, referable to the decomposition by heat which the solids undergo and the inferior solubility of the new products in the liquid.

\* Read November 8, 1884.

In §§ 238–241 *a* it was shown that the liquids triethylamine and water are remarkably more miscible when cooler than when warmer; and their relationship in this respect was pretty fully made out. The conclusion come to in this particular case was that, when the two liquids are brought together, a subcryohydrate is formed, and the heat attending (set free during) its formation may or may not be sufficient to effect its almost complete decomposition, or, rather, mitigate its formation according as the initial temperature of the two liquids is higher or lower. And that subsequent elevation of temperature affects decomposition. Depression of temperature promotes the formation of the subcryohydrate.

A liquid is in a different predicament from a solid when the question turns upon the solubility in a liquid medium. With a solid, increase of temperature always tends in the direction of fusion *per se*, which implies diminished cohesion and the bringing of the two (solid and liquid) into a community of physical state. In the case of two liquids, although, as before, rise of temperature may promote solution by diminishing cohesion, such promotion may be more than counterbalanced by the tendency of the increased heat to separate one or other liquid as a vapour, the particles of which, coalescing, form a liquid insoluble in the rest.

Be this as it may, it will be found that the separation of liquids from their mixtures by increase of temperature is by no means uncommon, and may be the rule rather than the exception long before temperatures approaching the critical ones are reached.

§ 257. *Change of Volume of Triethylamine and Water at about the Temperature of their Separation.*—The remarkable separation which takes place between triethylamine and water when a mixture of the two is warmed, and which was described in § 238, suggests the possible use of such a mixture as a calorimeter. For, if such separation is accompanied by any great change in volume, since the amount of additional heat required to effect a large separation is exceedingly small, a very exact measure of the heat given to the mixture by a given mass of matter cooling through a given range of temperature would be obtained by measuring such change of volume.

I accordingly took a bulb with a capillary stem and determined its capacity up to a lower mark on the stem, and then calibrated the stem. The capacity at  $16^{\circ}1$  was 9.1823 cubic centim. The mean volume of 1 millim. of the stem was .000830038 cubic centim., or 0.00009039 of the capacity of the bulb. Into this bulb 5.4873 grams of water were introduced and then 3.0600 grams of triethylamine, making a 35.8-per-cent. solution. The two on being mixed and brought to the temperature of  $16^{\circ}1$  had a volume which may be called V, and which was 9.1820 cubic centim. The bulb was now kept for an hour at each  $0^{\circ}5$  higher temperature. In the following Table the rise in millimetres for every  $0^{\circ}5$  is given; such rise being corrected for the calibration of the tube and corrected also for the expansion of the glass (cubic expansion .000026 for  $1^{\circ}$  C). The nearest tenths of millimetres only are given.

TABLE LVIII.

T.	Corrected increase on previous volume.	Corrected increase on original volume.	T.	Corrected increase on previous volume.	Corrected increase on original volume.
$16^{\circ}1$	millim.	millim.	$21^{\circ}6$	millim.	millim.
16.6	...	...	22.1	18.8	172.5
17.1	7.9	7.9	22.6	18.0	190.5
17.6	7.9	15.8	23.1	17.5	207.0
18.1	7.9	23.7	23.6	17.0	224.0
18.6	8.4	32.1	24.1	17.3	241.0
19.1	15.5	47.6	24.6	17.2	258.2
19.6	24.5	72.1	25.1	17.2	275.4
20.1	24.6	96.7	25.6	17.2	292.6
20.6	20.8	117.5	26.1	17.1	309.7
21.1	18.6	136.1	26.6	17.1	325.8
	17.6	153.7			343.9

The original volume at  $16^{\circ}1$  being 9.1820 cubic centim., at, for example,  $19^{\circ}1$  it was  $9.182 + 72.1 \times .00083001^*$ , or 9.2418 cubic centim. As the volumes in the third column are corrected for calibre, they serve at once to explain the behaviour of the liquid.

From § 237 it seems that the liquid here dealt with is, at starting, at  $16^{\circ}1$  a mixture of the suberyohydrate and the base itself. This mixture expands regularly from  $16^{\circ}1$  to  $17^{\circ}6$ . Through that range equal increments of temperature are accompanied by equal expansions. At  $18^{\circ}1$  the liquid

\* From table of calibration.



is opalescent, and that opalescence is accompanied by an increased expansion. At  $18^{\circ}6$  the liquid becomes quite milky, and on standing separates into two of nearly the same density and refractive index. These two are about equal in volume (see § 241 a). The two next half-degree warmings produce a still greater separation; I mean that the total actual sinking of the watery solution and the rise of the ammoniacal solution is probably greater in this case than before. The joint expansion has increased. Now this may be brought about by two causes: either that the separation is greater, or that after separation the mean expansion by heat of the separated parts together is greater. That the increased expansion is not due to the second of these causes seems proved by the fact that, as the heating is continued, the expansion—although, indeed, always greater than that at temperatures below the separating point—is less

Fig. 1.



than the expansion during separation. Separation produces some expansion; and this being superadded to the expansion due to the increased temperature of the separated constituents gives rise to the elegant curve of fig. 1. The lower and upper parts of this curve are straight lines at different inclinations to the axis. The region of separation is indicated by a curve tangent to both, and whose mean tangent is more inclined than either to the axis of percentage.

Although, therefore, the separation of the mixed liquids into two immiscible liquids (each of which is mixed) is accompanied by an abnormal volume-change (increase), this increase is not so much larger than the increase attributable to mere heat-dilatation as to make the liquid even at the brink of its critical condition especially valuable as a calorimeter.

Another resource would be of course to measure the degree of separation approximately by measuring the height of the plane of separation of the two immiscible mixed liquids heated by a known mass cooling through a known range. This would be indeed in theory a very effective calorimeter; but I do not see the way at present to overcome certain practical difficulties of arrangement and manipulation.

§ 258. *Diethylamine and Water*.—These two liquids appear to mix in all proportions at all atmospheric temperatures above  $0^{\circ}\text{C}$ . An aqueous solution of the base, when heated in an open vessel, gives off the base as a vapour, and the temperature does not rise above  $100^{\circ}\text{C}$ .

Into a strong glass tube, which was afterwards sealed, was introduced a mixture consisting of 45.42 per cent. of diethylamine and 54.58 per cent. of water. On heating this in an oil-bath, with a thermometer, very gradually, and again letting the temperature fall slowly, the bath being kept well stirred, the following changes were observed:—

At  $130^{\circ}$  the liquid was still quite clear.

$134^{\circ}\cdot 5$  separation was incipient.

$135^{\circ}$ . The lower layer amounted to about  $\frac{1}{5}$  of the whole.

$136^{\circ}$ .       "       "       "        $\frac{1}{4}$        "

$140^{\circ}$ .       "       "       "        $\frac{2}{7}$        "

$145^{\circ}$ .       "       "       "        $\frac{1}{3}$        "

$150^{\circ}$ .       "       "       "        $\frac{1}{3}$        "

$160^{\circ}$ .       "       "       "        $\frac{1}{3}$        "

The conditions were not such as to allow of exact measurement. The critical temperature is, however, trustworthy ; and the result shows that, within a range of about  $10^{\circ}$  C. only, the separation begins and is completed, as far as the completion is faithfully measured by the height of the plane of demarcation. It is to be noted that, owing in part to the refractive index of diethylamine being nearer that of water than is the refractive index of triethylamine, the above separation is not marked by the milkiess which characterizes the separation of the latter body \*. If it were not for accidental dust-particles floating on the surface of the lower liquid it would be, in some cases, almost impossible to distinguish the two layers. As the phenomenon of separation is one which has to be watched for, the tubes cannot be enclosed in metal cases for the purpose of equalizing the pressure on the glass. Although only one tube of this series has burst, I have not cared to carry the temperature above  $180^{\circ}$  C., which must correspond to a pressure of about 15 atmospheres.

TABLE LIX.

Separation between Diethylamine and Water as Liquids.

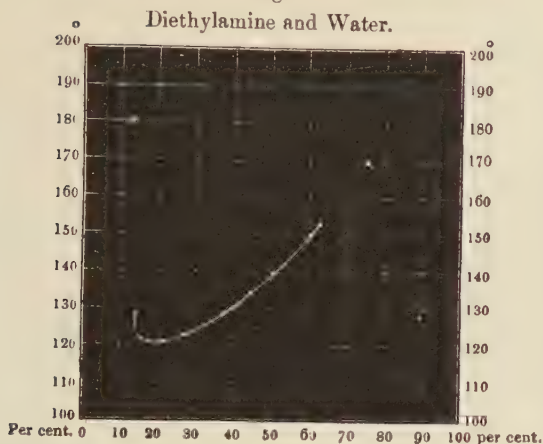
Diethylamine per cent.	Water per cent.	Temperature at which separation begins.
12.64	87.36	Still clear at ..... $180^{\circ}$ .
15.02	84.98	Begins to separate at $128^{\circ}$ .
16.30	83.70	" " $121.8$ .
20.94	79.06	" " $121$ .
26.89	73.11	" " $123$ .
37.80	62.20	" " $128$ .
45.42	54.58	" " $134.5$ .
62.35	37.65	" " $154$ .
75.76	24.24	Still clear at ..... $170$ (burst about $180^{\circ}$ ).

\* Mr. Illingworth, a student in my physical laboratory, has been kind enough to determine the refractive indices of this group

Ethylamine	.... $\frac{\rho}{1.3718}$
Diethylamine	.... $1.3850$
Triethylamine	.. $1.3999$

The determinations were made at  $17^{\circ}$  C., a temperature rather perilously near the boiling-point of ethylamine.

Fig. 2.



A few points are noticeable in these experiments. The 12·64-per-cent. solution showed no true separation at 180°. On standing to cool, with the point of the tube a little above the oil, a layer was formed on the liquid surface of about 1 millim. in thickness. This layer subsisted even when the temperature of the bath had sunk to 100°, provided the tube was not shaken. On repeating the experiment, and removing the tube from the bath at 180°, it became evident that the phenomenon was one of distillation. The upper and partly empty end of the tube being the first to cool, the liquid of highest vapour-tension, namely the diethylamine, distilled into that region, condensed, and floated on the heavier and more aqueous portion. Such a layer is rather apt to be overlooked, but its growth may be watched in comfort after the temperature has fairly begun to sink.

§ 259. It should also be remarked that while a 12·64-per-cent. solution at 180° has only a slight etching-action on glass, the 62·35-per-cent. solution caused the surface of the glass (soft German) to peel off in visible scales when heated to 150°–160°, acting like a caustic alkali. This may be the reason of the bursting of the 75·76-per-cent. tube, which had a wall-thickness of 2·5 millim. and an internal diameter of 9 millim. It is well to remember, therefore, that a tube which has withstood a pressure due to a certain temperature may afterwards give way when even at a lower one.



§ 260. I have not succeeded in separating ethylamine from water by heat in closed vessels. But by the closest analogy we must expect both that body and ammonia itself to leave the water with which they are combined as suberyohydrates (§§ 235, 233); and at some very high temperature and pressure to exhibit nearly complete insolubility with that liquid. All of these liquids contract with water and evolve heat.

§ 261. *Tetrethylammonium Oxide*.—Looking on aqueous ammonia as being a solution in water of the oxide  $\text{NH}_4 \text{HO}$ , the comparison between ethyl-, diethyl-, and triethyl-ammonium oxides on the one hand, and tetrethyl-ammonium oxide on the other, in regard to their solubilities in water being affected by heat, should present many points of interest both to the physicist and to the chemist. The following experiment may be noted; for although it brings us but little further in the immediate direction of our inquiry, it confirms the statement that a solution of tetrethylammonium is decomposed on concentration by evaporation. A 10-per-cent. solution heated in an oil-bath to  $180^\circ$  gives off a permanent gas which ultimately may burst the tube. This is no doubt olefiant gas. At the same time oily drops which float are formed in the tube; on cooling, they disappear. This is evidently triethylamine containing water; the reaction being



And it appears that this known decomposition is brought about by heat alone without concentration.

§ 262. *Tetramethylammonium Oxide* (a 10-per-cent. solution) does not show any separation at  $200^\circ$ , but begins to solidify at  $-16^\circ$ . The tetrethyl compound of the same strength also solidifies in an ice-salt cryogen.

§ 263. *Ethyllic Ether* may be here mentioned as a liquid which, though only slightly soluble in water, forms with it a solution decomposable by heat. Water saturated with ether at a given temperature, and heated in a closed tube a few degrees, becomes visibly milky. When such a solution is heated to  $100^\circ \text{C.}$ , the ether, probably nearly anhydrous, forms a distinct layer on the top. It is redissolved on cooling. Now in § 104 it was shown that ether united with water. In § 274 it will be shown that such union is accompanied by the

liberation of heat and by contraction. Here we have the third term of such relationship, namely, the decomposition of the combination by a rise of temperature.

§ 264. *Alcohol and Bisulphide of Carbon.*—It may be recalled that in §§ 207–228 strong, almost perfect, analogies were established between water-salt alloys and salt-salt alloys. So, now, I am led to consider the case of the mixture of two liquids neither of which is water. And in choosing for my first experiments alcohol and bisulphide of carbon, I was guided by the fact that, speaking from a chemical point of view, we should not expect there to be any relationship, and because both liquids can be got in a state of very great purity. The alcohol was obtained by distilling the nominally “absolute” from quicklime. The bisulphide was washed with water and distilled from oil of vitriol. A preliminary experiment showed that expansion resulted on mixing the two. A quill-tube about 4 feet long was closed at one end and half filled with the bisulphide; about an equal volume of alcohol was added. The tube was closed and the contents mixed. When the whole had resumed the air-temperature, a permanent lengthening of the column of about 11 millim. had taken place.

For exact determination the following method was employed. Two bulbs, A and B, nearly equal, were blown on a piece of thermometer-tubing of rather large bore (about 1 millim. internal diameter), the neck between the bulbs having the same width and being as short as practicable; the bulbs being weighed, bisulphide was introduced through a very fine capillary tube, until the lower bulb was filled at  $17^{\circ}6$ . The whole was again weighed. The upper bulb and the lower part of the stem being filled with alcohol, the height  $f$  was noted at which the liquid stood at  $17^{\circ}6$ . A third weighing followed. On tilting and frequently inverting, the two could be perfectly mixed. When brought again to  $17^{\circ}6$ , the height  $g$  was observed. The volume of the capillary from

Fig. 3.



$f$  to  $g$  is got by measuring the length, and weighing a column of mercury which has a length (exactly measured) of about the length  $f-g$ .

Actual weight of bisulphide . .	1.8180 gram.
„ „ alcohol . . .	1.9856 „
Reduced expansion (at $17^{\circ}6$ ) .	0.02912 cub. cent.

This gives an expansion of 0.007405 of the original joint volume. The method is seen to be one capable of extreme accuracy, and is, I think, though more laborious, preferable to a specific-gravity method, because the temperature is better under control. This individual result has, however, no special numerical significance, because the two liquids are not in any simple relationship by weight or volume, and because, as we should expect and as we shall see is the case (§ 271), the ratio of change of volume depends upon the ratio of the constituents.

It is important to note that the increase in volume here observed is accompanied by a fall in temperature, which at first, and until the temperature is recovered, tends to reduce the volume. This, the natural corollary of expansion, will be examined later.

§ 265. Alcohol and bisulphide of carbon mix with one another in all proportions at all temperatures between  $0^{\circ}$  and  $100^{\circ}$  C. This fact does not seem to be generally known, the reason perhaps being that a very small quantity of water prevents the perfect mixture taking place between some proportions of the nominal constituents. The examination of the simultaneous reciprocal solubilities of the three bodies alcohol, bisulphide, and water would be a fascinating inquiry, but a very onerous one; for many thousand experiments would have to be performed in order to trace the effect of even a few variations in temperature and in the threefold ratio. Moreover, the complication would be much further increased by the chemical attitude between alcohol and water.

§ 266. I made nine mixtures of alcohol and bisulphide containing the two liquids in different ratios. The liquids were weighed in tubes closed at one end, and having capillary necks, which were then sealed off. These solutions, when used, were transferred to open tubes, which were then cooled in an ordinary ice-salt cryogen with the following results.

TABLE LX.

Separation of Alcohol and Bisulphide of Carbon by Cold.

Per cent. of bisulphide.	Per cent. of alcohol.	Temperature at which separation begins.
94.94	5.06	Remains clear down to $-18^{\circ}4$ .
89.54	10.46	Becomes turbid at ..... $-14^{\circ}4$ .
84.89	15.11	" " ..... $-15^{\circ}9$ .
79.96	20.04	" " ..... $-16^{\circ}1$ .
65.11	34.89	" " ..... $-17^{\circ}7$ .
59.58	40.42	Remains clear down to $-20^{\circ}$ .
49.91	50.09	
39.96	60.04	
29.92	70.08	

In these experiments, as the thermometer sinks it is noticed that at several degrees above that at which separation begins the liquid becomes opalescent, or rather fluorescent; for in this state it is still perfectly transparent, and colours the transmitted light of a light orange-yellow. It is pale blue by the fluoresced light. On reaching the critical temperature of true turbidity, the change is abrupt. At only the fraction of a degree lower the liquid divides into two with surprising suddenness and precision. In the case of the 79.96-per-cent. mixture the volumes of the two separated liquids are about equal at  $-17^{\circ}$ , although at  $-15^{\circ}$  only the above-mentioned fluorescence betrays the impending change. The suddenness of the change argues that the quantity of heat lost during the change is inconsiderable. Again, on removing from the freezing-mixture and shaking up, I have not been able to detect anything like a stationary thermometer during remixture, although all analogy shows that there must be a tendency that way. Indeed the phenomenon closely resembles that described in §§ 238-241a attending the decomposition of an aqueous solution of triethylamine. But it is here presented with a falling thermometer, there with a rising one. Here it resembles the separation of a solid salt containing water of crystallization from an aqueous solution which still retains some: there it was due to the decomposition by heat of a subcryohydrate. Here the original mixing absorbed heat, as when a salt dissolves in water: there it liberated heat. Here such mixing gained volume: there it lost volume. The one case is, as it were, a real image of the other, and inverted, because real.

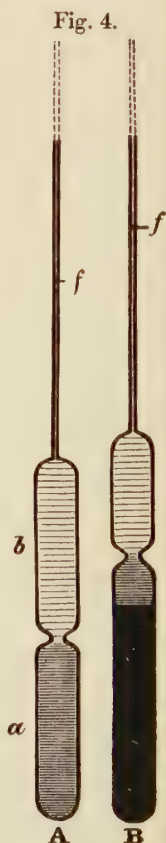


Only such a little bit of this behaviour is revealed by an ice-salt cryogen that it would be almost useless to draw its curve from these four points. Laid out in percentages of alcohol from left to right, it seems as though its shape would be like that of the reflexion in the axis of percentages of the curve of diethylamine and water (fig. 2).

*Alcohol, Bisulphide of Carbon, Amylene, Ether, Chloroform, and Benzol.*

§ 267. Perhaps we may take the relationship between alcohol and bisulphide of carbon as being typical of such a relationship as resembles the solution of nitre in water, or of fused nitre in fused nitrate of sodium (§ 220) (which results in expansion of the solidified alloy), or, lastly, the solubility of fused nitre in water under pressure (§ 252). The method of experimenting adopted reveals, however, somewhat unexpected relationships between other liquids, which relationships are of a more chemical character. Many chemists have of late years made great use of the term "saturation," and the expression has been of some real service. But its unguarded use has, I venture to say, given rise to some misconception. The word itself certainly conveys something absolute and complete; and it is undoubtedly intended to convey such an idea, especially when prefixed by "perfect" or contrasted with "partial." It is only necessary to revert to the types of physical saturation upon which the analogies of chemical saturation are based, to show that such condition is relative and not absolute. Chemical saturation is not a remote analogue of electric neutrality, and the latter is clearly relative.

§ 268. Two or three tubes were made, similar in principle to that of fig. 3, but of more general use (fig. 4). In one of these the lower and upper bulbs (up to a subsequently marked point on the stem) were of absolutely the



same capacity (between 3 and 4 cub. cent.). In the second the lower bulb was several times as big as the upper. By adding weighed quantities of mercury to the lower bulb, the ratio of contents could be changed at will.

In order to give an idea of the absolute and relative dimensions, I may state that in one of the tubes the exact capacity of  $a$  and  $bf$  at  $17^{\circ}6$  was  $3.3777$  c. c., the total volume upon which the expansion or contraction took place being therefore  $6.7554$  c. c. The mean volume of 1 millim. of the capillary tube about  $f$  was  $0.00140183$  c. c.; so that 1 millim. on the capillary meant  $0.00020737$  of the joint liquid volumes. As the readings could be made by means of a cathetometer\* to within  $0.2$  millim., I imagine that the numerical results are strict to the fifth decimal place. The only other sources of error appear to be the mixing of the liquids during the filling of the upper bulb and capillary. The filling of both bulbs is effected by means of a funnel-capillary, which reaches about half way down into the bulb which has to be filled. Accidental soiling of the tube is removed by a thin German-silver cotton-covered wire.

In the following Table equal volumes at  $17^{\circ}6$  of the liquids enumerated were taken. There is in every case an expansion marked  $+$ , or a contraction marked  $-$ . Before these signs is  $H$ ,  $C$ , or according as heat is liberated or absorbed. Immediately beneath these signs is the amount of contraction upon one volume of the original liquids taken jointly (before mixture). Below these is the temperature to which the altered volume has to be brought in order to restore it to the original (joint) volume.

The experimental errors appear here to be entirely due to (1) the diffusion during the second filling of the two liquids against gravity, an operation which lasts about 15 minutes, and (2) the imperfect purity of the substances. The first of these is quite negligible, as the common surface is only about 1 square millimetre, while the volumes are over 3 cubic centimetres.

\* Designed and made by the "Cambridge Scientific Instrument Company."

TABLE LXI.  
Equal Volumes at 17°·6.

	Alcohol.	Ether.	Bisulphide of Carbon.	Amylene.	Chloroform.	Benzol.
Alcohol .....	0	$\left\{ \begin{array}{l} \text{H}- \\ \cdot 006894 \\ 23^{\circ} \cdot 5 \end{array} \right.$	$\left\{ \begin{array}{l} \text{C}+ \\ \cdot 007278 \\ 11^{\circ} \end{array} \right.$	?	$\left\{ \begin{array}{l} \text{H}- \\ \cdot 002488 \\ 19^{\circ} \cdot 75 \end{array} \right.$	$\left\{ \begin{array}{l} \text{C}+ \\ \cdot 0002488 \\ 17^{\circ} \cdot 42 \end{array} \right.$
Ether .....	.....	0	$\left\{ \begin{array}{l} \text{C}+ \\ \cdot 001556 \\ 16^{\circ} \cdot 5 \end{array} \right.$	$\left\{ \begin{array}{l} \text{H}- \\ \cdot 0004977 \\ 18^{\circ} \cdot 1 \end{array} \right.$	$\left\{ \begin{array}{l} \text{H}- \\ \cdot 0108869 \\ 25^{\circ} \cdot 8 \end{array} \right.$	$\left\{ \begin{array}{l} \text{H}- \\ \cdot 00346308 \\ 20^{\circ} \cdot 4 \end{array} \right.$
Bisulphide of Carbon .....	$\left. \begin{array}{l} \text{ } \\ \text{ } \end{array} \right\}$ .....	.....	0	$\left\{ \begin{array}{l} \text{C}+ \\ \cdot 00311055 \\ 15^{\circ} \cdot 05 \end{array} \right.$	$\left\{ \begin{array}{l} \text{C}+ \\ \cdot 00688468 \\ 11^{\circ} \cdot 7 \end{array} \right.$	$\left\{ \begin{array}{l} \text{C}+ \\ \cdot 0069469 \\ 11^{\circ} \cdot 1 \end{array} \right.$
Amylene ...	.....	.....	.....	0	$\left\{ \begin{array}{l} \text{H}- \\ \cdot 0015138 \\ 19^{\circ} \cdot 1 \end{array} \right.$	$\left\{ \begin{array}{l} \text{C}+ \\ \cdot 0010783 \\ 16^{\circ} \cdot 6 \end{array} \right.$
Chloroform	.....	.....	.....	.....	0	$\left\{ \begin{array}{l} \text{C}+ \\ \cdot 00183969 \\ 15^{\circ} \cdot 9 \end{array} \right.$
Benzol .....	.....	.....	.....	.....	.....	0

In taking the tube out of its bath it is tilted, bulb upwards, so as to be at an angle of about 45°. Where the differences of refractive index and of density are great, complete mixture seems to be reached in five or six reversals of a few minutes each\*. But in none of the cases given above were the reversals less than 20 in number nor of less duration than 10 minutes each, nor was the manipulation stopped before trial showed that constancy of volume had been reached. Each experiment from first to last takes about five hours. The open end of the capillary may be stopped by a short piece of caoutchouc-tubing containing a glass plug.

\* In making such experiments as these, the question presents itself—If two colourless (or similarly coloured) liquids have the same refractive index, how shall we know whether they are mixed or not? And if, therewith, they have the same density, how does their emulsion differ at all from their mixture? It is, indeed, unlikely that any two liquids have the same refractive indices or the same density at more than one temperature. And that they should have both refractive index and density alike at more than one temperature involves an improbability of a higher order. Apart from this, however, it is likely that the skin of a liquid has a different (higher) density and a higher refractive index than the mass of the same liquid. (F. G., Phil. Mag. November 1883.)

§ 269. Returning to Table LXI., a cloud of ideas suggest themselves. The results are obtained on equal volumes at an arbitrary temperature  $17^{\circ}6$  both before and after mixture. Wherever there is gain of volume, there is absorption of heat, cold, diminished heat-tension (C). Wherever there is loss of volume, there is liberation of heat, heating, increased heat-tension (H). These thermal effects are only given qualitatively in the Table, and were actually obtained in a second series of experiments made as follows. Equal volumes of the two liquids were run from burettes into two test-tubes of thin glass, one of about twice the capacity of the other. The narrower was put inside the wider, and both put into water at  $17^{\circ}6$ . After sufficient standing, a thermometer in the inner liquid marks nearly the same temperature. The tubes are removed from the water and wiped, the inner one broken through at the bottom and used as a stirrer.

Let us consider, now, two of these cases more exactly, in one of which there is heat and contraction, in the other cold and expansion.

### *Ether and Chloroform.*

#### *Maximum Rise of Temperature.*

§ 270. The liquids were weighed instead of being measured; otherwise they were treated as in § 269, with the exception that two experiments were made in each case; in the second experiment the thermometer-bulb was brought to the temperature shown in the first experiment before being used.

TABLE LXII.

Showing Rise of Temperature from  $17^{\circ}6$  on mixing Ether and Chloroform in different proportions by weight.

Ether.	Chloroform.	Rise in temperature.
	Per. cent.	
2	1 or 33.33	8.0
1	1 " 50.00	11.0
1	1.615 " 61.8	11.7 ( $C_4H_{10}O : CHCl_3$ )
1	2 " 66.66	11.5
1	3 " 75.00	10.9
1	4 " 80.00	9.6

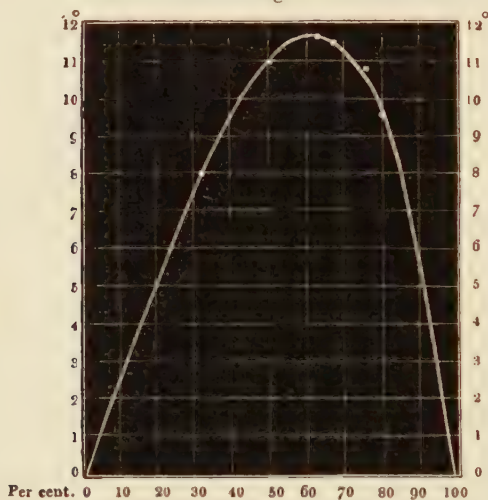
As we are here merely searching for a maximum, we may



neglect certain effects which would be of the utmost importance under other circumstances. Thus the specific heat of none of the liquids is the same, and each rise of temperature given is weighted with the specific heat of the liquid in which it takes place. But I believe I am right in assuming that this effect would not in this instance materially shift the place of the maximum, although it would alter every one of the individual numbers, and that not in the same proportion.

The curve, fig. 5, shows the relationship of increased heat-

Fig. 5.



tension to the proportions of chloroform and ether by weight by which it is caused.

From these six experiments, therefore, we find that the greatest change (rise) of temperature takes place when the liquids are in the proportion of 1 ether to 1.615 of chloroform by weight, which is the proportion of  $C_4H_{10}O$  to  $CHCl_3$ .

§ 271. This method of experimentation, however, does not allow of such great accuracy as the method of change of volume. If it be found that the greatest change of volume takes place when these weight-ratios (1 ether to 1.615 of chloroform) are mixed, and that a very small change of ratio either way diminishes the change of volume, this evidence will be much strengthened towards the conclusion that the relationship is indeed between molecule and molecule.

Taking, therefore, the tube like A (fig. 3), having equal bulbs of 3·2325 c. c., I put 9·304 grams of mercury into the lower bulb. This reduced the capacity of the lower bulb 0·693 c. c., bringing it to 2·5390, the upper bulb by 3·2325. They are in the ratio of 1·380 to 1·084, which, again, are in the ratio of the molecular volumes (molecular weights divided by specific gravities) of the two liquids. The ratio-value of the capacity of the calibrated capillary-stem has now, of course, to be taken upon a lesser total volume—namely, upon 5·7715 instead of upon 6·4650. The first quantities of chloroform added should be shaken and warmed with the mercury, so as to displace the film of air between the mercury and the glass, or some dissolved gas. If this is not done before the ether is added, air-bubbles arise when the two are mixed, and vitiate the readings.

The result for equimolecular volume at 17°·6 is 0·0116756: chloroform 1, ether 1·2731.

Instead of 9·304, I now introduced only 9·0 grams of mercury; this reduced the lower bulb 2·5699 c. c., and the two together to 5·8024; the volume-ratio between the two being 1 chloroform to 1·258 ether. The shrinkage on the new volume was 0·0114783.

Next I introduced 9·6 grams of mercury. This reduced the lower bulb to 2·5241 c. c., and the two together to 5·7566. The volume-ratio between the two is now 1 chloroform to 1·2806 ether. The shrinkage on the new volume was 0·015706.

TABLE LXIII.

VOLUMES.		On being mixed and brought to the same temperature (17°·6) which they had before mixture, shrink to the below-given fraction of the joint volume they had before mixture.
Chloroform.	Ether.	
Per cent.	Per cent.	
50·00	50·00	·0108869
44·29	55·71	·0114783
43·99	56·01	·0116756 (C <sub>4</sub> H <sub>10</sub> O, CHCl <sub>3</sub> )
43·83	56·17	·0115706

The table shows the great accuracy of which this method is capable, and discovers a maximum contraction exceedingly close to, if not at, the monomolecular ratio ; thus confirming the result got by the cruder method of increased heat-tension, § 270.

The liquid solidifies to a white crystalline mass at a constant temperature below  $0^{\circ}$ , which I shall give when I have determined it exactly.

It seems, then, that ether and chloroform unite chemically with one another to form the body  $C_4H_{10}O$ ,  $CHCl_3$ , a substance which may be analogous in its composition with  $S_2Cl_4 \cdot 2(C_4H_{10}O)$ .

*Vapour-tension of Chloroform and Ether Mixtures.*

§ 272. The result of the experiments given above will make it imperative to revise previous ideas about the vapour-tension of mixed liquids. The following experiments with ether and chloroform show how the vapour-tension varies with the composition. The absolutely pure and dry substances were mixed in various proportions by weight, and each mixture was introduced into one of a series of perfect barometers in a room of uniform temperature. The barometers stood in the same trough close together. The readings were made with a cathetometer at a distance of nine feet. The readings were made backwards and forwards through the series three times. The atmospheric pressure was made constant by adjusting the mercury in the trough. About five grams of the liquid were introduced into each tube, and in all cases enough, as shown by a rough measurement and calculation, to ensure there being far more than sufficient of each kind of liquid to supersaturate. After determining the mercurial depression, the liquid columns above the mercury were measured, and their specific gravities assumed to be those due to mixture without change of volume. This is not quite true (see § 268). Further, it is assumed that the liquid has the same composition before as after its introduction into the tube. This, also, is not quite exact. Neither of these errors has been taken into account in the following Table ; for they are both of them negligible in comparison with the numerical data sought.

TABLE LXIV.

Vapour-tensions of Mixtures of Chloroform and Ether.

T = 19°·02.

Chloroform, per cent. by weight.	Ether, per cent. by weight.	Mercurial depression.	Liquid above mercury.	Vapour-tension in millim of mercury at 19°·02.
100	0	200·0	84·0	190·7
90	10	205·2	87·2	196·0
80	20	222·3	106·5	211·7
70	30	236·2	104·0	226·4
63	37	240·2	79·2	233·1
(C <sub>4</sub> H <sub>10</sub> O, CHCl <sub>3</sub> ) 61·76	38·24	243·9	85·0	236·4
60	40	248·5	81·2	241·4
50	50	285·0	83·3	278·2
40	60	318·7	85·2	312·2
30	70	349·8	77·5	344·8
20	80	383·2	81·8	377·9
10	90	413·8	83·9	408·8
0	100	442·6	90·0	437·8

§ 273. The increase of vapour-tension as the proportion of ether increases is therefore continuous, but by no means regular. There is in the neighbourhood of the monomolecular ratio a diminution in the rate of increase; but immediately this region is past, the curve becomes rectilinear. As the barometer-tubes stand side by side in a row, they present a very interesting appearance, as the mercurial levels form a curve closely similar to that in fig. 6, A (p. 271) turned upside down. Guided by heat-development and shrinkage, we have therefore detected the existence of C<sub>4</sub>H<sub>10</sub>O, CHCl<sub>3</sub>, and showed that the vapour-tension confirmed the existence of this body. Are we, then, to assume that in every case in Table LXI. where there is heat-development and shrinkage, there is also true chemical union? Reluctant as some may be to admit to the title of chemical compounds a class of bodies which probably numbers many thousands, there seems no help for it. There can be but little doubt, for instance, that ether unites with alcohol and benzol, that chloroform unites with alcohol and with amylene, and so on. The experiments necessary for the proof of this assertion will be laborious, and will require such care



and concentration that I must again invite other workers into this fertile field. There is, however, one point which may be here noted. Two elements may unite to complete saturation in respect of one another, yet the molecules so formed may be quite prepared to unite as a whole with another atom or molecule (compare § 267).

§ 274. The contraction and heating attending the mixing of alcohol and water have been long known. When, in § 98, I described the solid combination of the two,  $C_2H_6O, 4H_2O$ , and called it a cryohydrate (I should now call it a subcryohydrate), I did not suppose that it was only one of so numerous a family as appears to be the case. In § 104 was briefly described a combination of ether with water. I may here mention the circumstance that equal volumes of the two, when shaken together at  $17^{\circ}1$ , rise in temperature to  $18^{\circ}9$ . Equal volumes brought together at  $17^{\circ}6$  in the experimental tube of § 268, and agitated by a globule of mercury being made to pass to and fro through the capillary opening, contract 0.005436 of their joint volume, and require to be heated to regain that volume. This contraction is probably very far from the maximum, as there is no doubt a large quantity of passive matter present. For the same reason, the maximum liberation of heat will probably be found with a less water-ratio. Where the maximum heat-liberation occurs we should look for the subcryohydrate, and there also for the maximum contraction.

*Vapour-tensions of Mixtures of Bisulphide of Carbon and Ether.*

§ 275. Taking next an instance where expansion and cold result from mixture, I give at once the numerical results as to the vapour-tensions of the various mixtures.

TABLE LXV.

Vapour-tensions of Mixtures of Bisulphide of Carbon and Ether.

T = 18° 88 C.

Bisulphide of Carbon, per cent. by weight.	Ether, per cent. by weight.	Mercurial depression, in millim.	Liquid above mercury, in millim.	Vapour-tension, in millim. of mercury, at 19° 02.
100	0	291·9	78·1	284·5
90	10	353·3	77·5	346·3
80	20	380·8	75·0	374·3
70	30	404·1	82·8	387·3
60	40	416·5	81·2	410·1
50	50	425·2	80·0	419·3
40	60	441·0	90·9	424·6
30	70	434·8	75·0	429·8
20	80	438·1	83·4	433·0
10	90	437·2	81·7	432·5
0	100	436·5	81·7	432·1

Specific gravity of ether, 0·72 ; of bisulphide of carbon, 1·23.

§ 276. Laid out graphically we get accordingly the curve B, fig. 6. Perhaps the most notable character of this curve is its descent at the upper right end. This means that, although bisulphide of carbon has a lower vapour-tension than ether, a little bisulphide loosens the ether and raises the vapour-tension. The effect on the vapour-tension of the liquid brought about by the addition of a little ether to the bisulphide is much more marked.

*Vapour-tensions of Mixtures of Chloroform and Bisulphide of Carbon.*

§ 277. Referring again to Table LXI. it is seen that, with whatever of the liquids there examined bisulphide of carbon is mixed, expansion occurs and the temperature is lowered. With chloroform these results are very marked ; and having examined the relationship between bisulphide and ether and between chloroform and ether, let me describe the relationship between chloroform and bisulphide of carbon.

TABLE LXVI. *a*.

Vapour-tensions of Mixtures of Chloroform and Bisulphide of Carbon.  $T = 16^{\circ} \text{C}$ .

Chloroform, per cent. by weight.	Bisulphide of Carbon, per cent. by weight.	Mercurial depression, in millim.	Liquid above mercury, in millim.	Vapour-tension, in millim. of mercury, at $16^{\circ}$ .
0	100	269.9	53.1	264.8
3	97	271.8	53.2	266.2
5	95	277.5	74.9	270.4
10	90	271.6	57.8	266.1
15	85	272.3	56.2	266.8
20	80	273.0	61.9	266.9
30	70	270.7	70.7	263.7
40	60	265.8	60.2	259.7
50	50	260.3	61.3	254.0
60	40	249.6	56.0	243.7
70	30	241.0	60.0	234.6
80	20	227.9	60.5	221.4
90	10	215.4	80.8	206.6
100	0	176.2	64.6	169.2

Spec. grav. of bisulphide of carbon, 1.23; of chloroform, 1.49.

§ 278. On laying these numbers out graphically, the curve C, fig. 6, presents itself. Although we are dealing here with millimetres, the shape of the curve towards pure bisulphide of carbon required confirmation. I therefore employed a temperature of nearly  $2^{\circ} \text{C}$ . lower; and having prepared fresh examples of the liquids with equal care, and having changed the barometer-tubes, I found:—

TABLE LXVI. *b*.

Vapour-tensions of Mixtures of Chloroform and Bisulphide of Carbon.  $T = 13^{\circ} \text{C}$ .

Chloroform, per cent. by weight.	Bisulphide of Carbon, per cent. by weight.	Mercurial depression, in millim.	Liquid above mercury, in millim.	Vapour-tension, in millim. of mercury, at $13^{\circ}$ .
0	100	259.5	83.0	251.6
5	95	266.0	108.1	255.7
10	90	260.3	91.0	251.5
15	85	258.5	85.2	250.3
20	80	255.5	70.9	248.6
30	70	252.5	70.9	245.4
40	60	248.0	73.3	240.6
50	50	243.5	83.0	235.0
60	40	236.1	78.2	227.8
70	30	220.3	59.5	214.0
80	20	210.7	76.5	202.3
90	10	199.1	78.1	190.4
100	0	170.0	113.2	158.4

Spec. grav. of bisulphide of carbon, 1.23; of chloroform, 1.49.

Fig. 6.

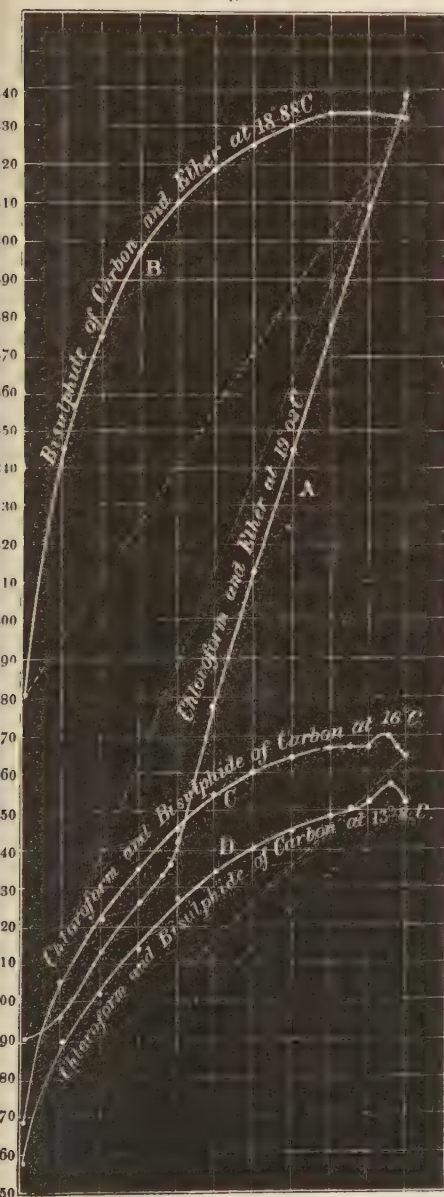
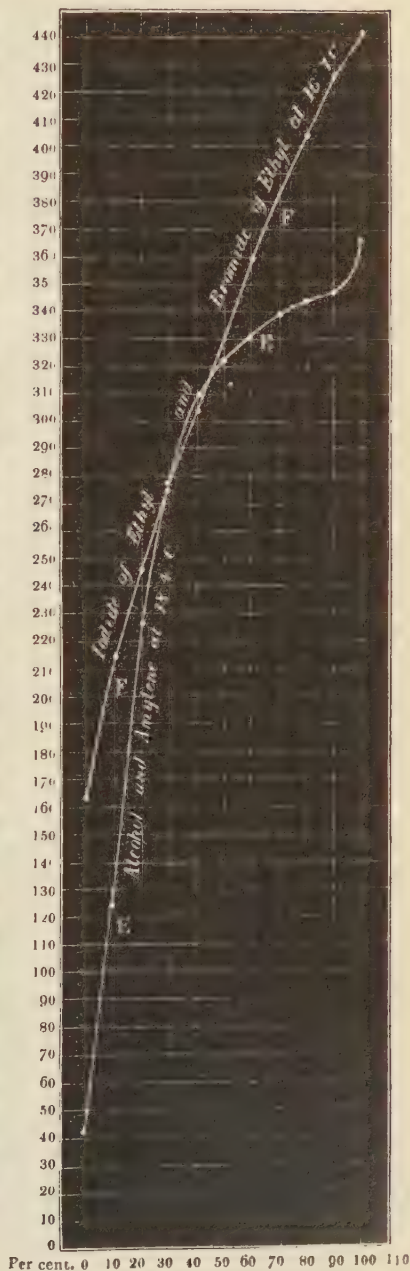


Fig. 7.





The result seems, then, to be this : The vapour-tension of bisulphide of carbon at  $16^{\circ}0$  is 264·8 millim., at  $13^{\circ}8$  it is 251·6 millim., both referred to mercury at those temperatures. Of chloroform the vapour-tensions at these two temperatures, also referred to mercury at the same temperature, are 169·2 and 158·4. A very great increase of the vapour-tension is brought about by mixing a very little bisulphide with the chloroform ; a little rise is brought about by mixing a little chloroform with the bisulphide. The graphic interpretations of the two Tables LXVI. *a* and LXVI. *b* are shown in curves C and D, fig. 6.

§ 279. If we could find two liquids showing neither contraction nor expansion when mixed, and neither liberating nor absorbing heat, the vapour-tension of a mixture of such liquids should be expressed by the equation

$$vt_{(ma+nb)} = vt_a + \frac{ma(vt_b - vt_a)}{ma + nb},$$

where generally  $vt_s$  means the vapour-tension of the liquid  $s$ , and where  $a$  and  $b$  are the liquids and  $m$  and  $n$  their respective masses. The vapour-tension curve would be a straight line joining the vapour-tensions of the constituents. The maximum departure from this straight line on the curves in fig. 6 gives us the maximum interference. This, in the case of chloroform and ether, is at the monomolecular ratio. Now, if we search the curve of mixtures containing bisulphide of carbon, we find there also a maximum departure from the mean at a certain ratio. In the case of bisulphide of carbon and ether this is at 30 or 35 per cent. of the ether (say 32·5). This implies that the maximum departure from the mean takes place where 1 molecule of ether ( $C_4H_{10}O$ ) is mixed with 2·02 molecules (say 2 molecules) of  $CS_2$ . At this ratio we may suppose there to be no indifferent or inert matter. If we consider chemical union to be due to an action of attraction, and regard the maximum thermal or volume effects as taking place when there is no superfluity of either constituent, so here we have an equally distinct molecular ratio, and an absolutely definite one (at all events at a given temperature), where a sort of anti-union takes place—a maximum effect of repulsion. This is a state of things for which some new nomenclature may be

necessary. There may be as many anticombinations as there are combinations; and the former may be quite as definite in weight-ratio as the latter. The essential difference is that, while attraction may result in the production of new stuffs, the latter has the locally opposite action.

Again, with chloroform and bisulphide the maximum departure from the mean is at 40 per cent. bisulphide. This signifies 1 molecule chloroform to 1·05 molecule bisulphide. I therefore submit these formulæ—



What is the relative nature of the bodies which should give a straight line on the vapour-tension curve of their various mixtures? Such may probably be found amongst hydrocarbons. I find that when equal volumes of ethylic and amylic alcohols are mixed at 13°·9, the temperature rises to 15°·1, implying the formation of a species of double alcohol. Referring to Table LXI. (§ 268) and to the few representative bodies there considered, we find that amylene and alcohol are almost without volume-change.

An examination of the vapour-tensions of their mixtures gave the following numbers :—

TABLE LXVII.

Alcohol, per cent.	Amylene, per cent.	Mercury.	L. C.	Sp. gr.	Cor- rection.	V.-T.
100	0	46·2	73	·79	4·3	41·9
90	10	129·8	99	·78	5·7	124·1
80	20	232·2	85	·76	4·8	227·4
70	30	282·1	85	·75	4·8	277·3
60	40	313·9	90	·73	4·9	309·0
50	50	329·0	98	·72	5·3	323·7
40	60	335·3	101	·71	5·3	330·0
30	70	339·6	100	·69	5·1	334·5
20	80	340·7	117	·68	5·9	334·8
10	90	344·1	121	·67	6·0	338·1
0	100	362·0	112	·66	5·5	356·5

T=18°·4 C. Spec. grav. of alcohol, ·79; of amylene, ·66.

The curve is seen in fig. 7, E (p. 271).

Through the favour of my colleague, Dr. Hodgkinson, I obtained some pure iodide and bromide of ethyl. These were

again washed, dried, and redistilled. The following Table shows the vapour-tensions of their mixtures. They were shielded from the light when in contact with the mercury.

TABLE LXVIII.

Iodide of ethyl.	Bromide of ethyl.	Mercury.	L. C.	Sp. gr.	Cor- rection.	V.-T.
0	100	459	65	1.40	6.8	452.2
10	90	439	100	1.45	10.8	428.2
20	80	415	88	1.50	9.8	405.2
30	70	389	74	1.55	8.6	380.4
40	60	372	93	1.60	11.1	360.9
50	50	343	87	1.65	10.7	332.3
60	40	316	76	1.70	9.6	306.4
70	30	286	73	1.75	9.6	276.4
80	20	260	98	1.80	13.1	246.9
90	10	227	88	1.85	12.2	214.8
100	0	172	62	1.90	8.8	163.2

$T=16^{\circ}.7$  C. Spec. grav. of bromide, 1.4; of iodide, 1.9.

The curve F, fig. 7, shows that the vapour-tensions of the mixtures of these two substances lie nearly in a straight line, and that the two substances therefore very closely fulfil the condition of absolute non-interference.

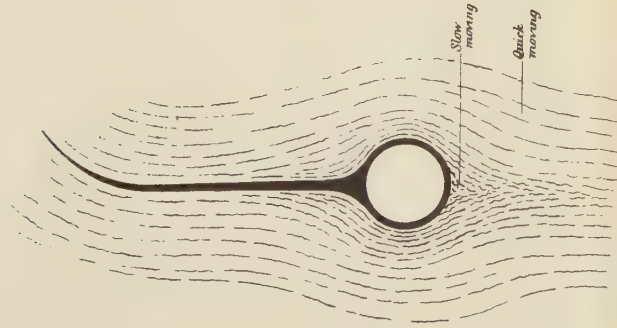


Fig. 1.

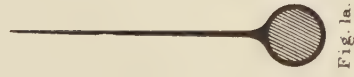


Fig. 1a.

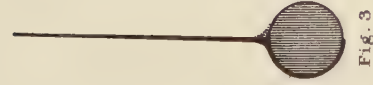


Fig. 3.



Fig. 4.

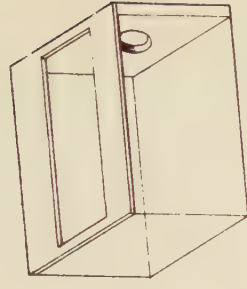


Fig. 5.



Fig. 6.



Fig. 2.

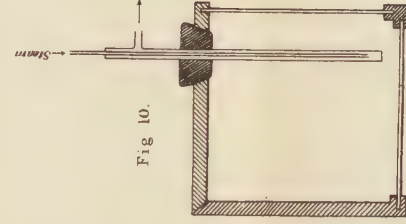
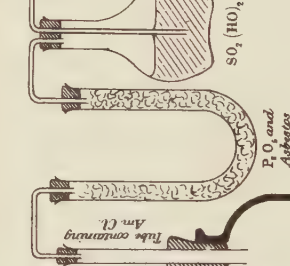


Fig. 10.

Sectional Plan.

Air, Hydrogen or  
Carbonic Anhydride

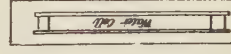


To Air Pump  
and  
Vacuum Gauge

Ca (Cl)

Tube containing  
Am. Cl.

Sectional Plan of Experimental  
Vessel, showing Gas connections.



Servo Electric  
Lamp.

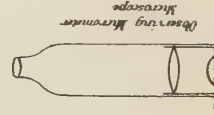


Fig. 8.

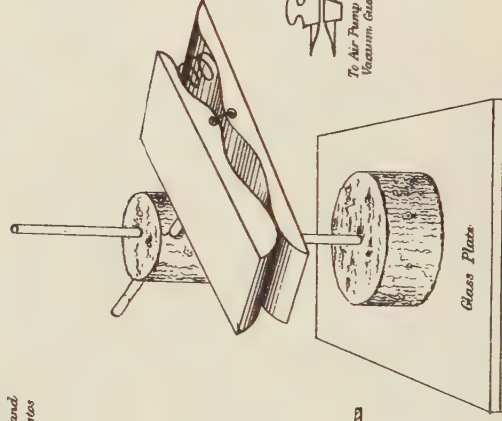


Fig. 7.

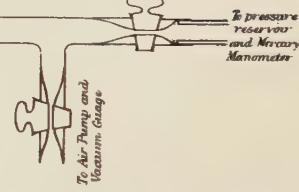
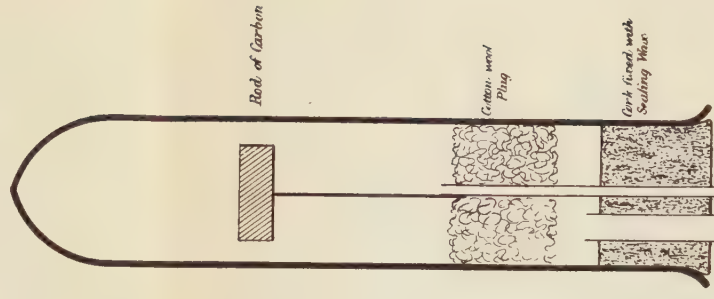
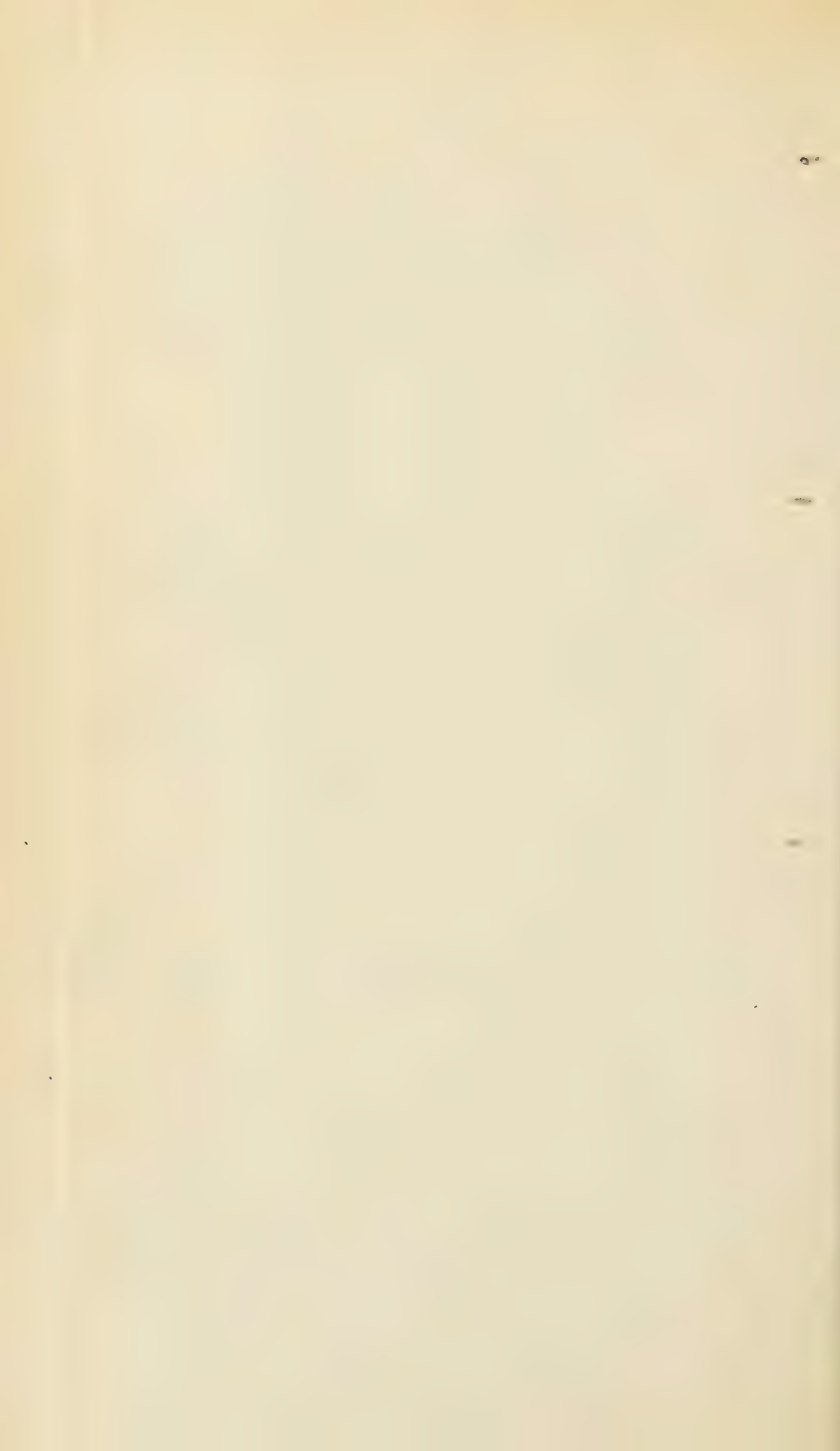


Fig. 9.



Exhaust for  
Sticks.





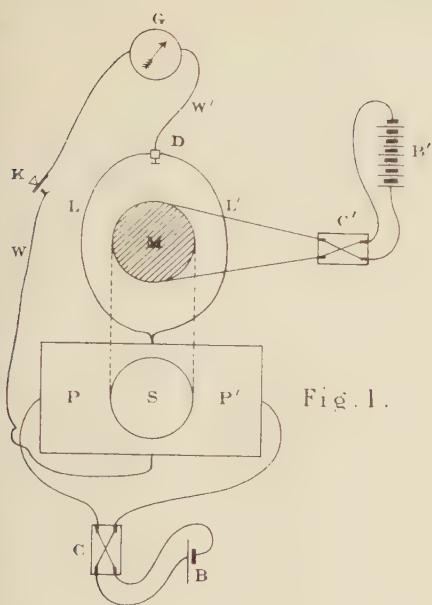


Fig. 1.

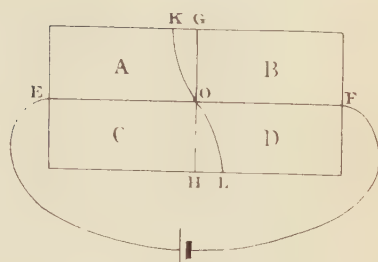


Fig. 4.

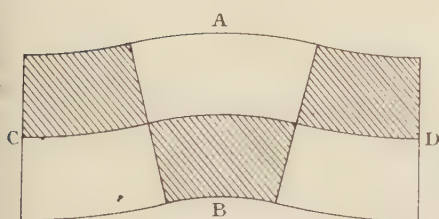


Fig. 3.

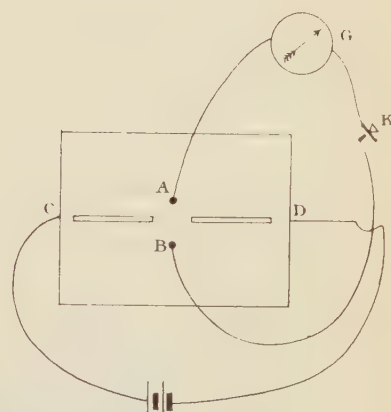


Fig. 5.

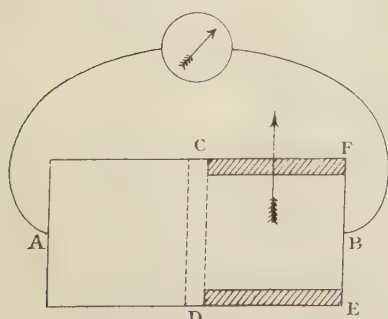


Fig. 2.

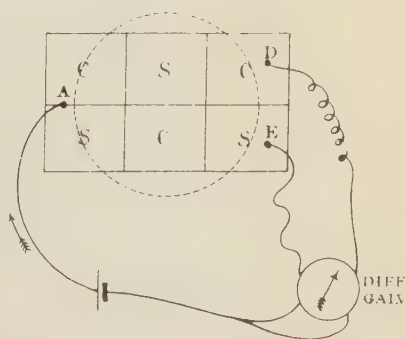


Fig. 6.



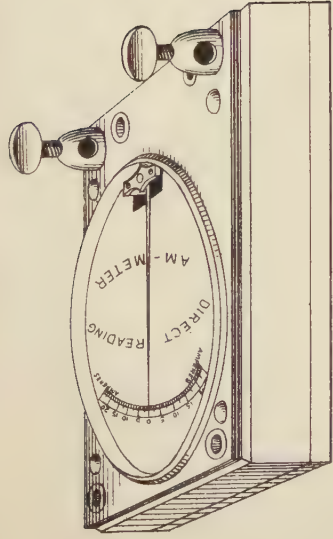


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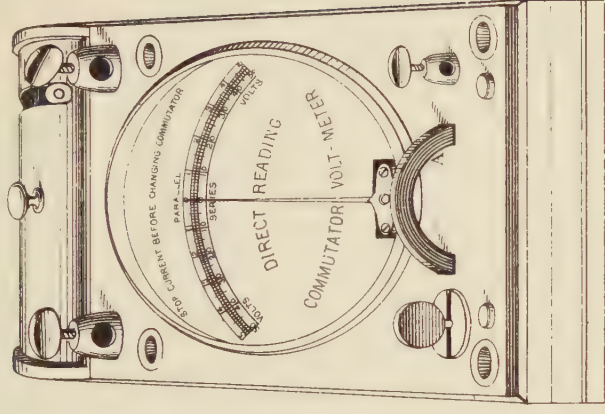


Fig. 2.

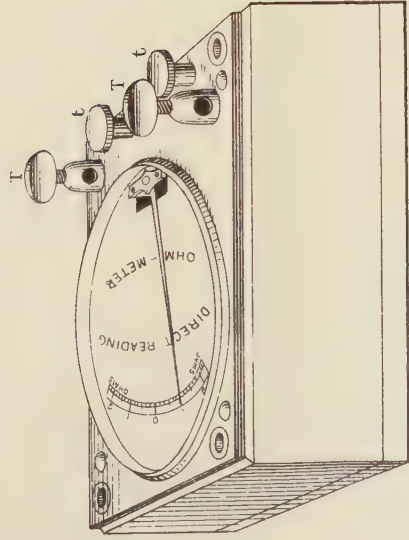


Fig. 3.

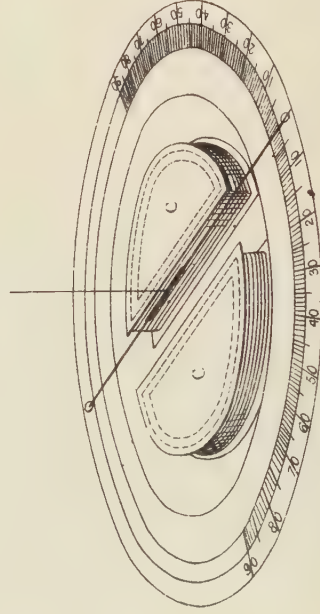


Fig. 4.

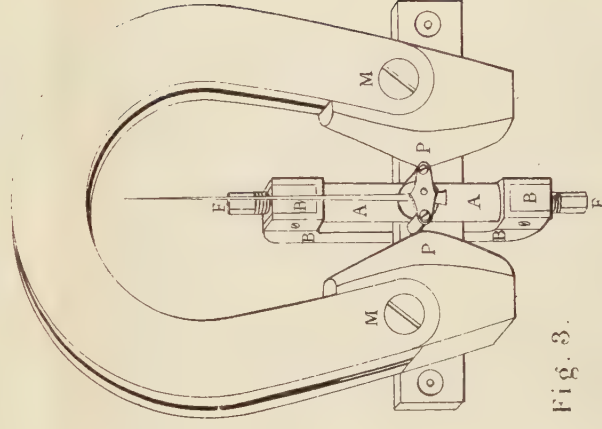


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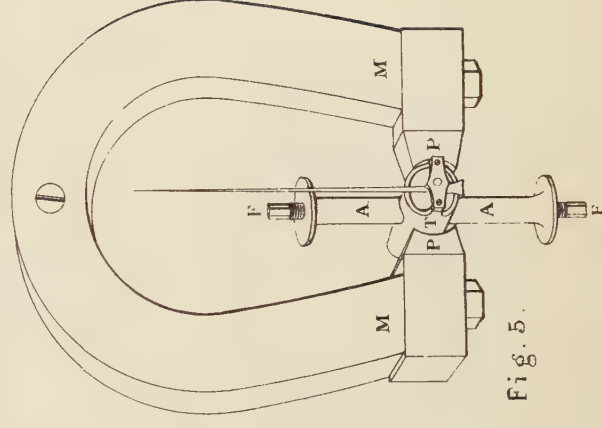


Fig. 6.

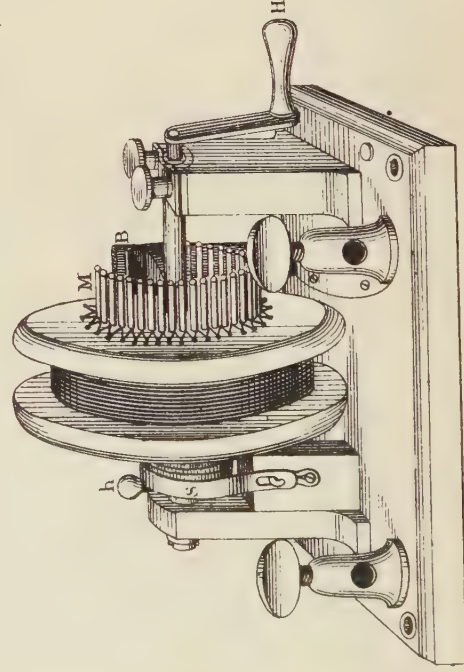


Fig. 7.





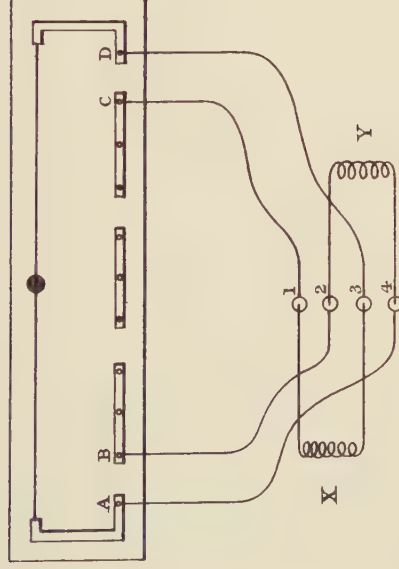


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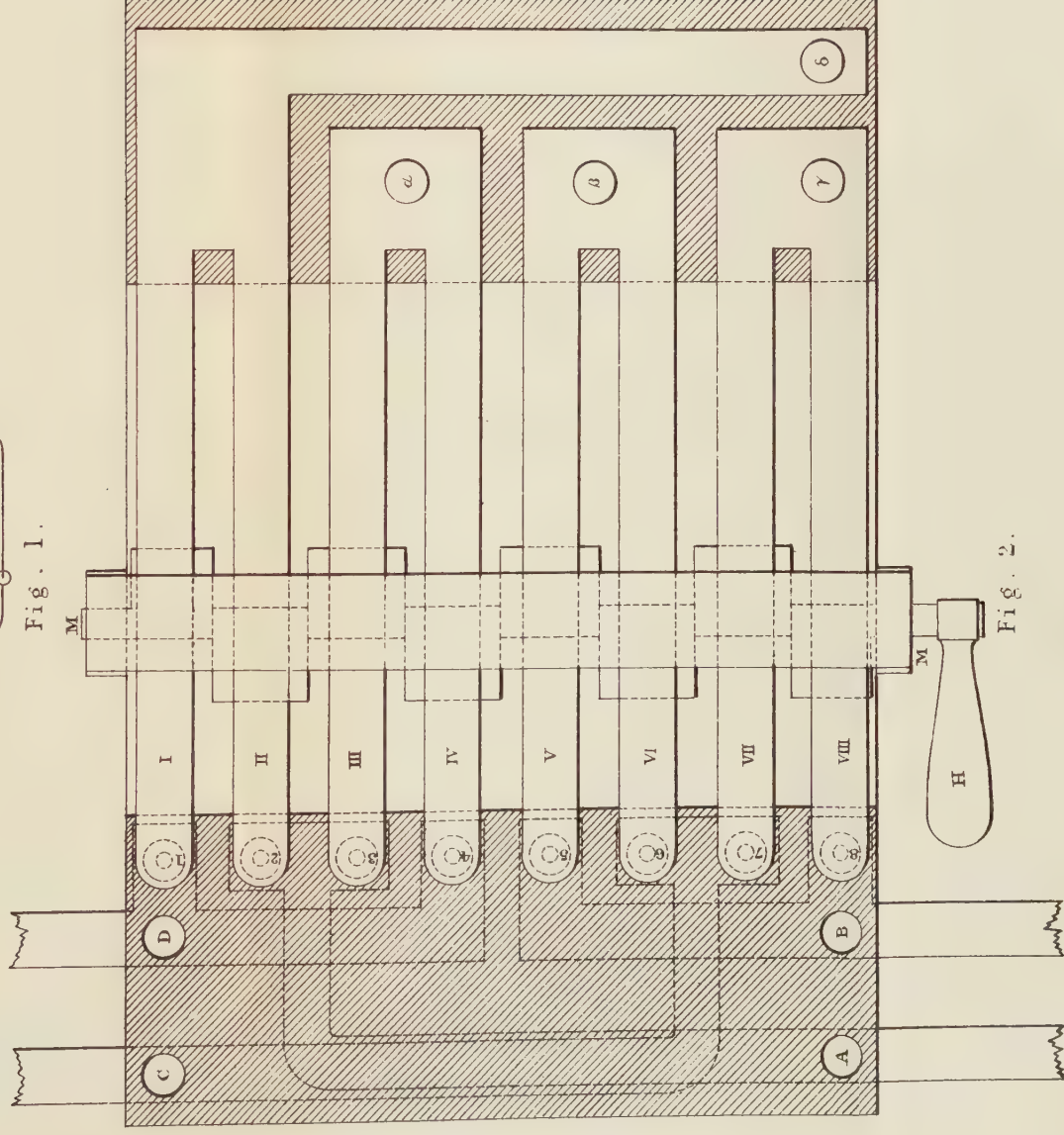


Fig. 2.

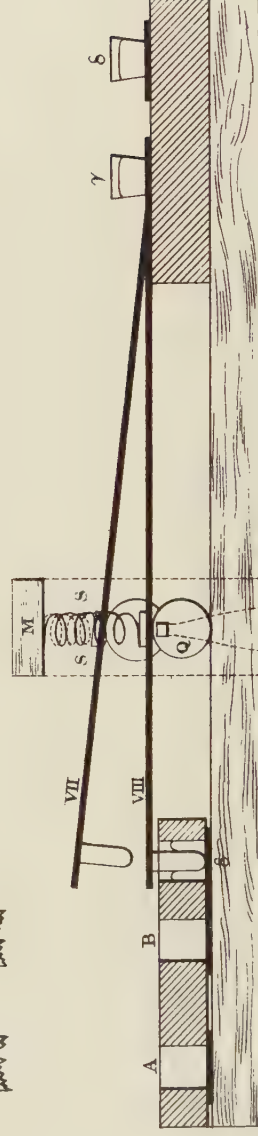


Fig. 3.

Muttern Bros. lith.



Fig. 1.

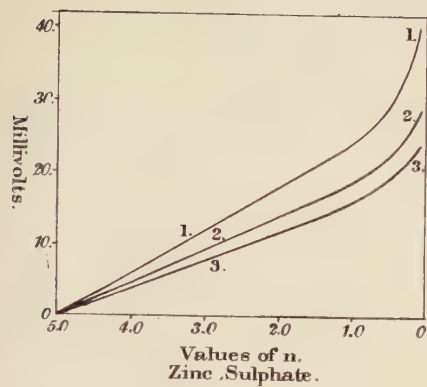


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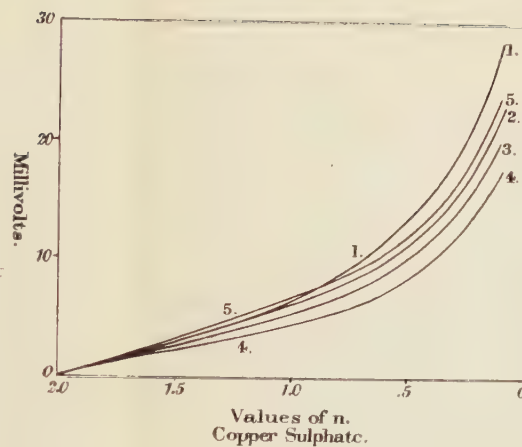


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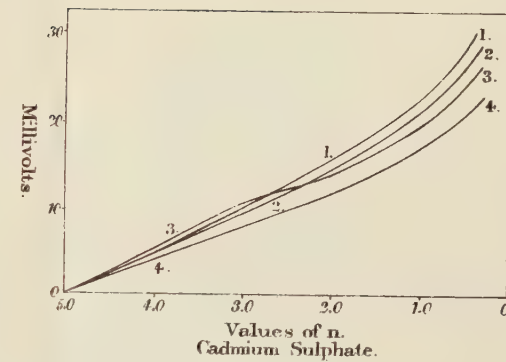


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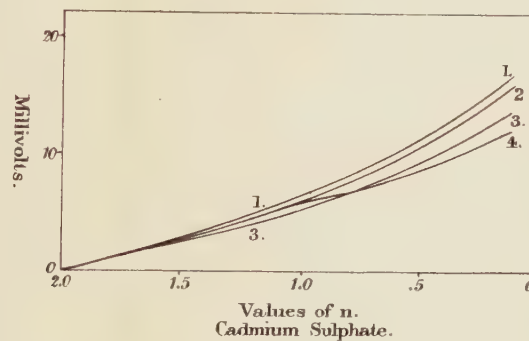


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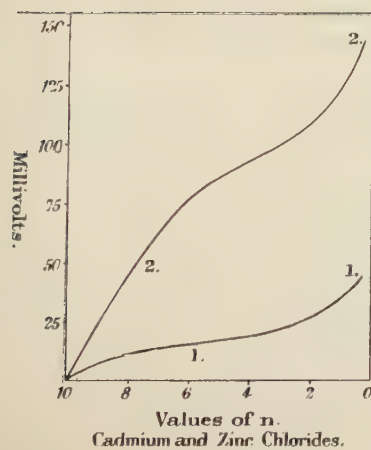


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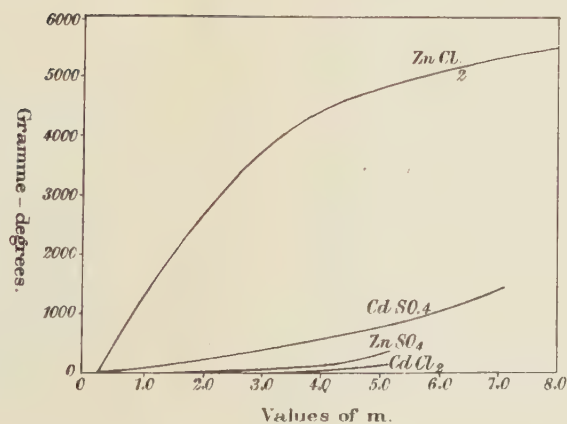
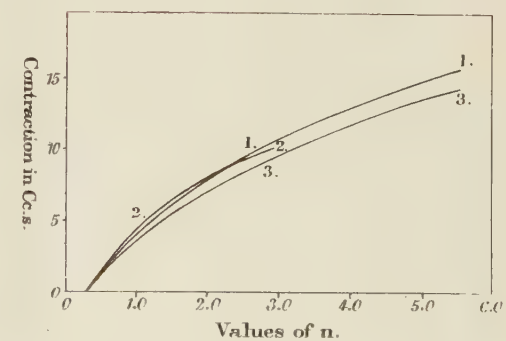


Fig. 7.







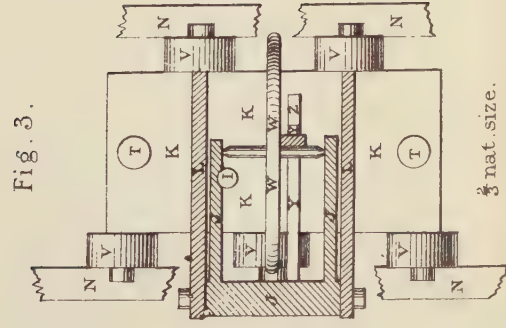


Fig. 3.

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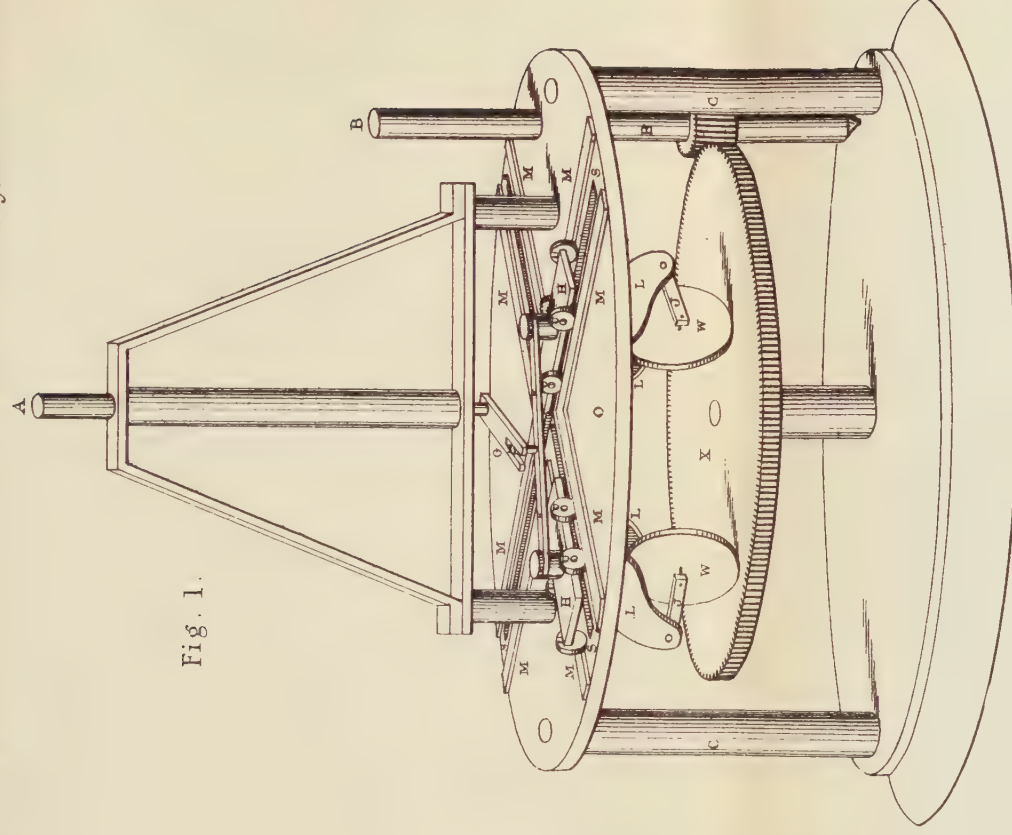


Fig. 1.

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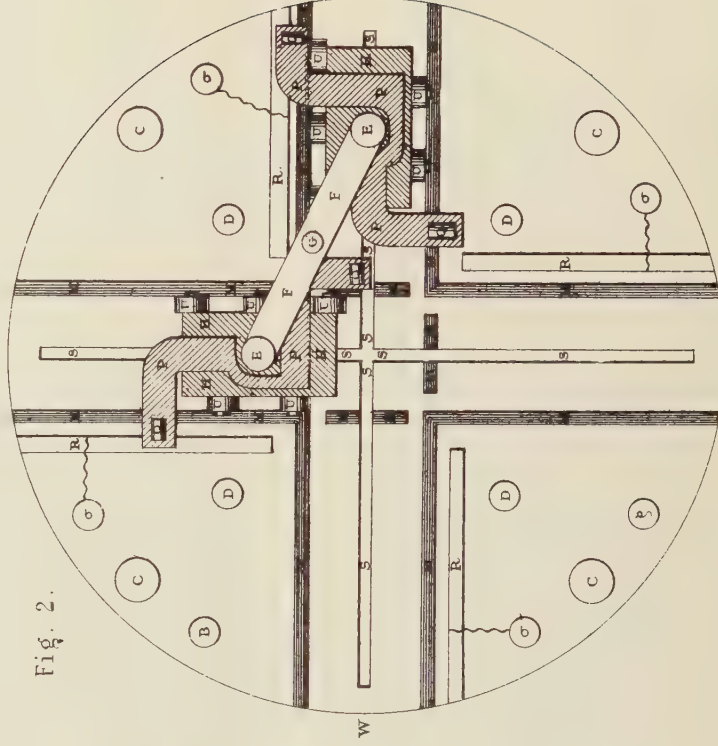


Fig. 2.

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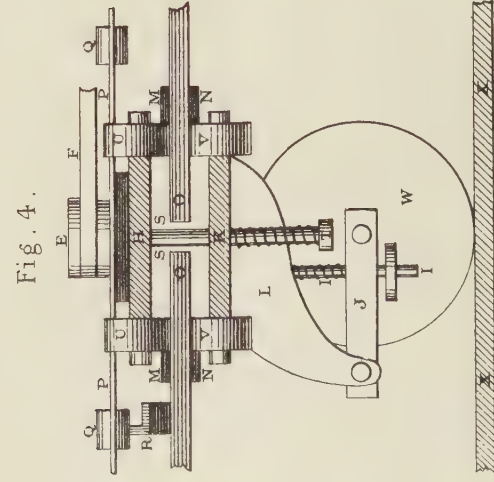
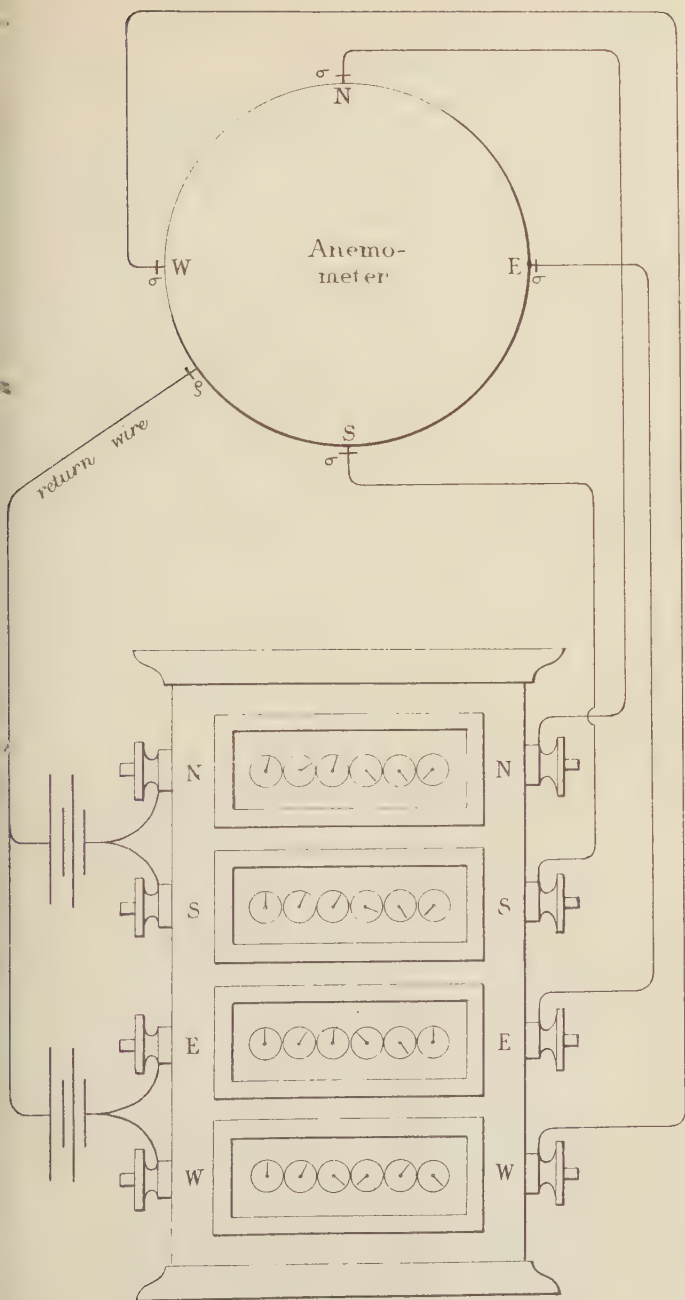


Fig. 4.

$\frac{3}{8}$  nat. size.





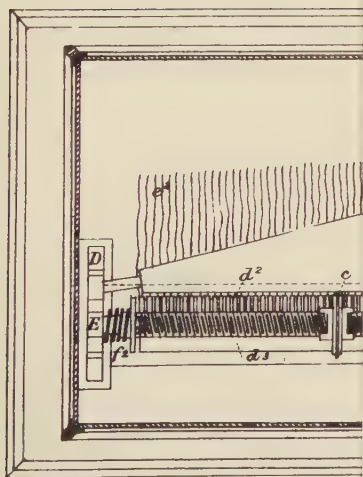
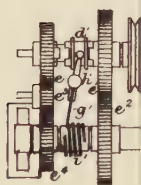
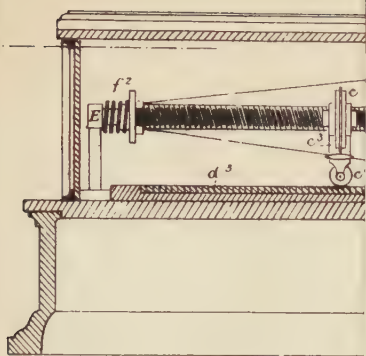
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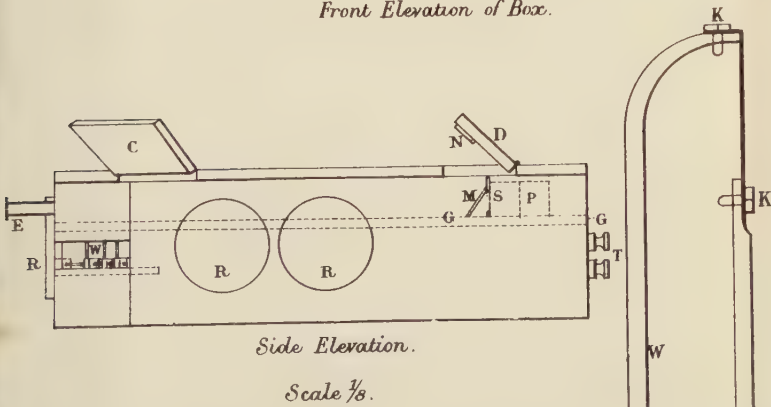
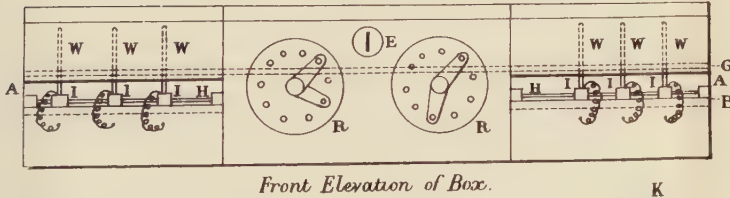
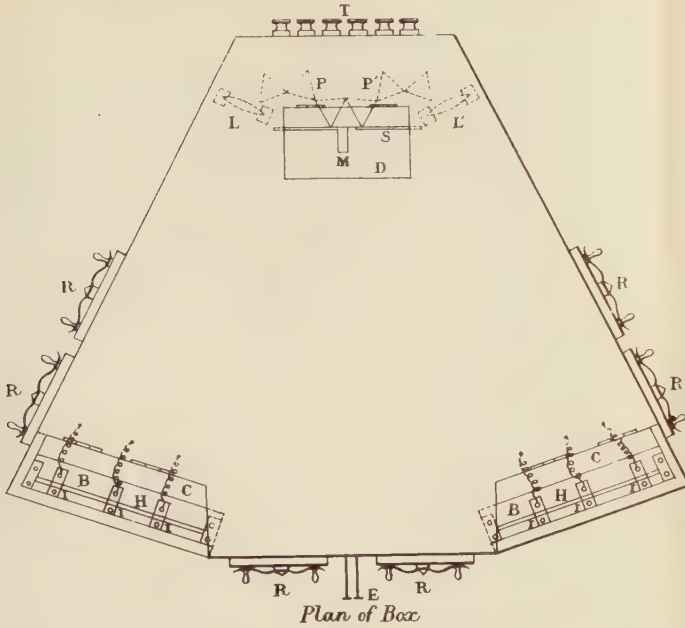




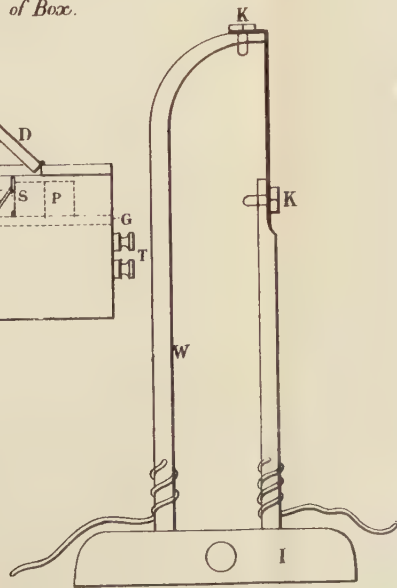


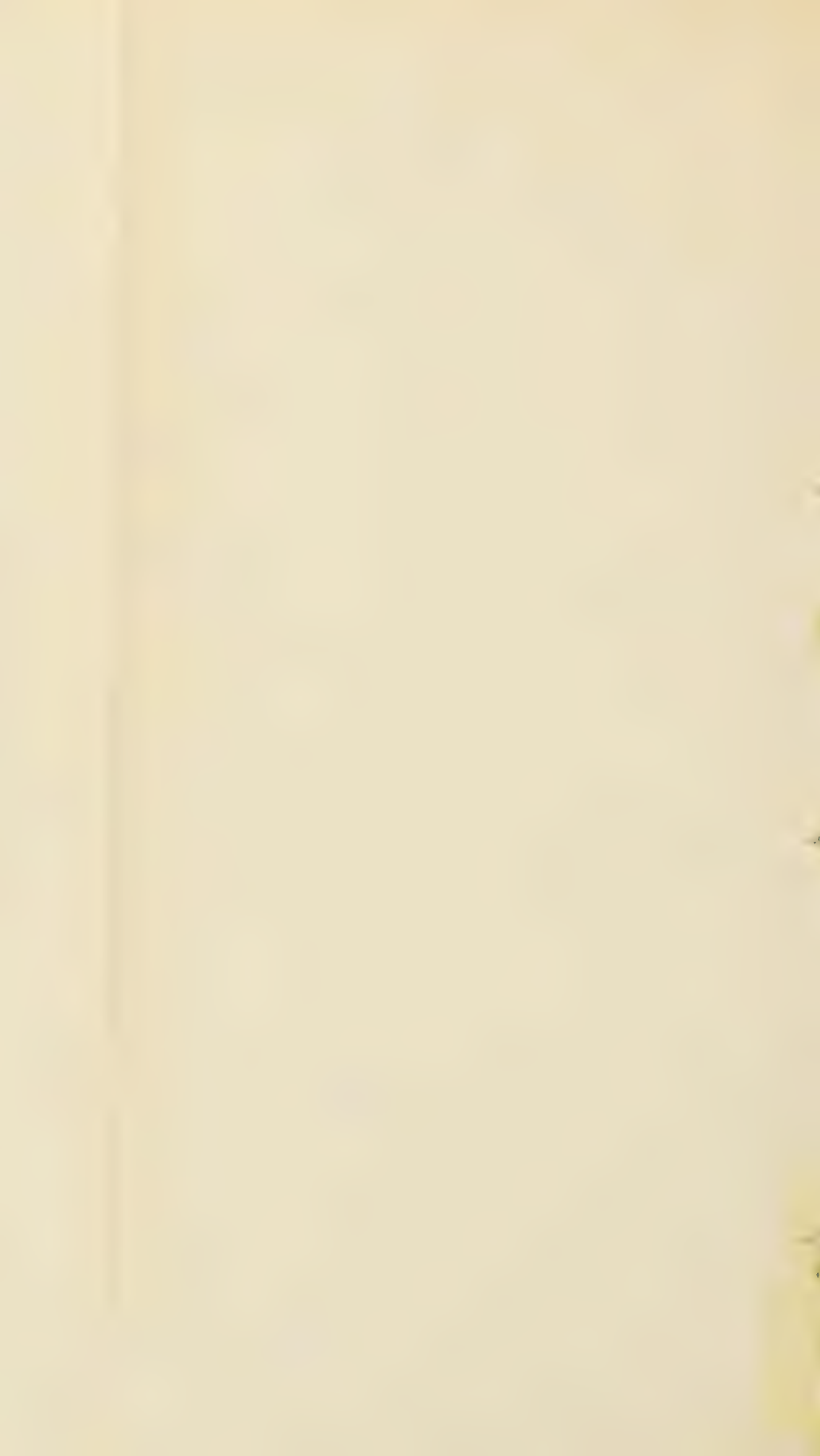


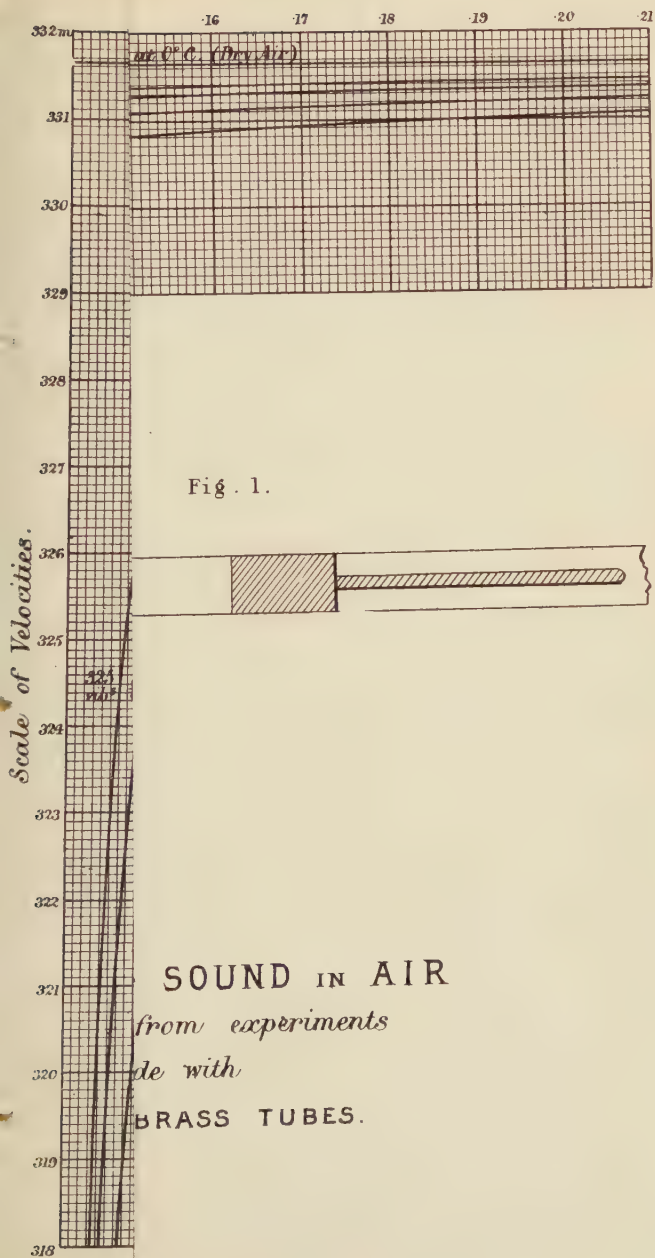
APPARATUS FOR COLOUR COMBINATIONS.



*Sliding frame carrying the incandescent wire. — Full size.*

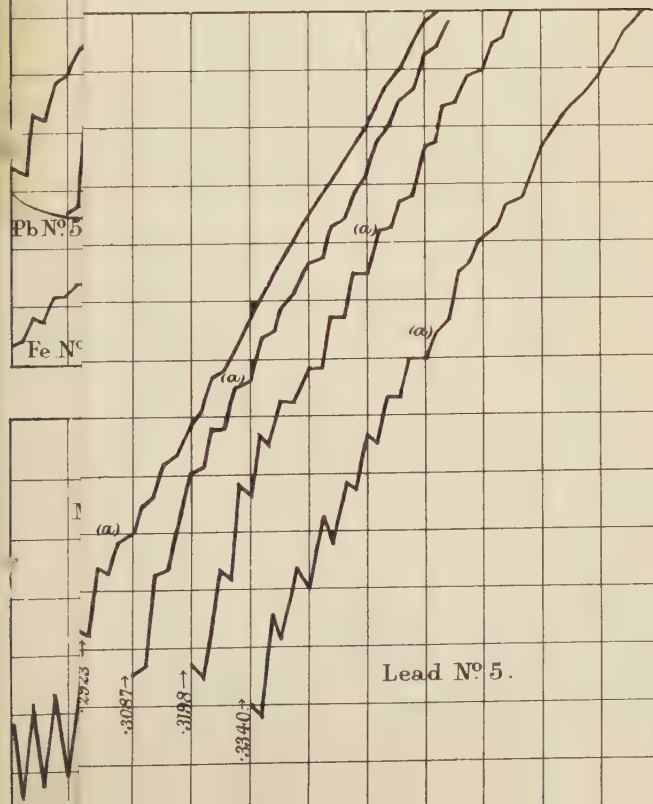
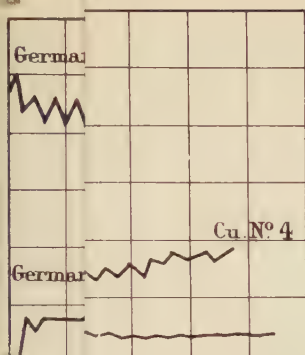














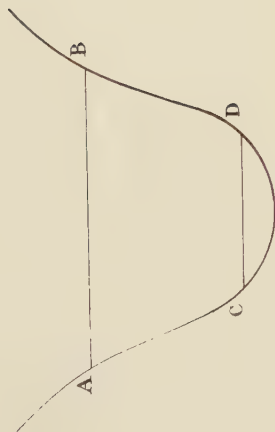
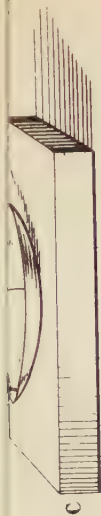


Fig. 3

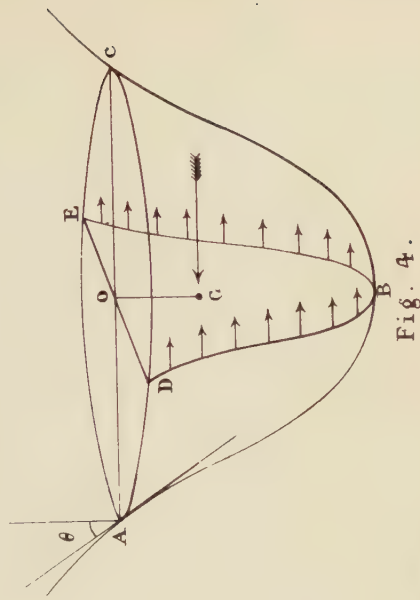


Fig. 4.

Mintern Bros. lith



PROCEEDINGS  
AT THE  
MEETINGS OF THE PHYSICAL SOCIETY  
OF LONDON.  
SESSION 1884-85.

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February 9th, 1884.

Dr. F. GUTHRIE, President, in the Chair.

The following communication was made :—

“On the Phenomena presented by Bodies when highly illuminated  
in Dusty Air.” By Dr. O. J. LODGE and Mr. J. W. CLARK.

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February 23rd, 1884.

Dr. F. GUTHRIE, President, in the Chair.

The following were elected Members of the Society :—

E. F. J. LOVE; JAMES GRUNDY; Rev. F. J. SMITH, B.A.;  
F. R. BARRELL, B.A.



The following communications were made :—

“On the Adjustment of Resistance-Coils;” and “On a Modified Resistance-Balance.” By Prof. S. P. THOMPSON.

“On the Difference of Potentials required to give Sparks in Air.” By Prof. G. CAREY FOSTER and Mr. A. H. FISON.

“On some Experiments with a Magnetized Watch.” By Prof. G. FORBES.

March 8th, 1884.

Dr. F. GUTHRIE, President, in the Chair.

The following communications were made :—

“On the Electrochemical Equivalent of Silver, and the Absolute E.M.F. of a Clark's Cell.” By Lord RAYLEIGH.

“Experiments illustrating an Explanation of Hall's Phenomenon.” By Mr. SHELFORD BIDWELL.

March 22nd, 1884.

Dr. F. GUTHRIE, President, in the Chair.

The following communications were made :—

“On an Explanation of Hall's Phenomenon.” By Prof. S. P. THOMPSON and Mr. C. C. STARLING.

“Note on Hall's Phenomenon.” By Mr. HERBERT TOMLINSON.

“On Hall's Effect in Tin.” By Mr. SHELFORD BIDWELL.

“On some Properties in Electromagnetics.” By Prof. S. P. THOMPSON and Mr. W. M. MOORSOM.

April 26th, 1884.

Dr. F. GUTHRIE, President, in the Chair.

The following were elected Members of the Society :—

RICHARD INWARDS, F.R.A.S.; ARTHUR PRINCE CHATTOCK.

The following communications were made :—

“On the Indicator-Diagram of a Gas-Engine.” By Profs. AYRTON and PERRY.

“On a Metrical Barometer.” By Dr. W. H. STONE.

May 10th, 1884.

The Meeting was held in the Mason College, Birmingham.

Dr. F. GUTHRIE, President, in the Chair.

The following were elected Members of the Society :—

W. STEPNEY RAWSON, M.A. ; Lieut. E. J. W. SLADE, R.N.

The following communications were made :—

“ On an Illustration of the Refraction of Waves.” By Prof. J. H. POYNTING.

“ On an Oxyhydrogen Lantern suitable for Lecture-experiments.” By Mr. C. J. WOODWARD.

“ On the Effect of Temperature on the Mixing of Liquids.” By Dr. F. GUTHRIE.

May 24th, 1884.

Prof. W. G. ADAMS, Vice-President, in the Chair.

The following was elected a Member of the Society :—

F. C. PHILLIPS.

The following communications were made :—

“ On Eutexia.” By Dr. F. GUTHRIE.

“ On an Immersion-Galvanometer ;” and “ On Kohlrausch’s Metre-Bridge for Alternating Currents.” By Dr. W. H. STONE.

“ On a Speed Indicator.” By Mr. W. T. GOOLDEN.

“ On a Speed Indicator.” By Mr. WALTER BAILY.

June 14th, 1884.

Dr. F. GUTHRIE, President, in the Chair.

The following was elected a Member of the Society :—

ARTHUR STANLEY BUTLER.

The following communications were made :—

“ On a new Apparatus for Colour-Sensations.” By Mr. H. H. HOFFERT.

“Experiments on the Velocity of Sound in Tubes.” By Mr. D. J. BLAICKLEY.

“On the Thermal Relationship of Water and certain Salts.” By Messrs. B. ILLINGWORTH and A. HOWARD.

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June 28th, 1884.

Dr. F. GUTHRIE, President, in the Chair.

The following was elected a Member of the Society :—

W. S. HEMSLEY.

The following communications were made :—

“On the Practical Use of the Silver Voltameter for the Measurements of Electric Currents.” By Lord RAYLEIGH.

“On a Colour-mixing Apparatus founded on Double Refraction.” By Lord RAYLEIGH.

“On a Phenomenon in Electromagnetic Induction.” By Mr. C. V. BOYS.

“On the Alterations in the Electrical Resistances of Metallic Wires, produced by Coiling and Uncoiling.” By Mr. J. HOPPS.

“On the Absolute Determination of the Electrical Capacity of a Condenser, and on a Method of finding the Period of Vibration of a Tuning-fork.” By Mr. R. T. GLAZEBROOK.

“On a Sunshine-Recorder.” By Prof. McLEOD.

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November 8th, 1884.

Prof. W. E. AYRTON, Vice-President, in the Chair.

The following was elected a Member of the Society :—

KAVARGEE DADABHOY NARGAMVALA.

The following communications were made :—

“On certain Phenomena attending Mixture.” By Dr. F. GUTHRIE.

“On certain Voltaic and Thermo-voltaic Constants.” By Dr. C. R. ALDER WRIGHT and Mr. C. THOMPSON.

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November 22nd, 1884.

Dr. F. GUTHRIE, President, in the Chair.

The following was elected a Member of the Society :—

JAMES BEASHER.

The following communications were made :—

“On the Permanence of some Electrical Standards;” “On some Experiments on the Effects of Moisture in modifying the Refraction of Plane-Polarized Light by Glass;” and “On a Spectro-Photometer.”

By Mr. R. T. GLAZEBROOK.

“Note on a Point in the Theory of Pendent Drops;” and “On a Capillary Multiplier.” By Mr. A. M. WORTHINGTON.

“On a new Solar Eyepiece.” By Mr. A. HILGER.

December 13th, 1884.

Dr. F. GUTHRIE, President, in the Chair.

The following communications were made :—

“On the Influence of an Electric Current on the Rate of Thinning of a Liquid Film.” By Profs. A. W. REINOLD and A. W. RÜCKER.

“On a Tuning-fork Interrupter and Commutator.” By Dr. W. H. STONE.

“On a new Oxyhydrogen Lantern-Microscope.” By Mr. LEWIS WRIGHT.

January 24th, 1885.

Dr. F. GUTHRIE, President, in the Chair.

The following were elected Members of the Society :—

A. HOWARD; J. C. McCONNEL, B.A.;

A. M. WORTHINGTON, M.A.; J. ROSE-INNES, B.Sc.

The following communications were made :—

“Lecture-Experiments on Spectrum Analysis.” By Mr. E. CLEMINSHAW.

“On an Instrument illustrating the Equilibrium of three Forces.” By Mr. WALTER BAILY.

“On the Poiograph.” By Mr. C. H. HINTON.

*Annual General Meeting.*

February 14th, 1885.

Prof. F. GUTHRIE, President, in the Chair.

The following Report of the Council was read by the President :—

In presenting their Annual Report the Council congratulate the Society on the valuable work which has been brought before the Meetings during the past year in the 43 separate Communications which have been made. New subjects for investigation have been brought forward by our President's papers on Alloys and Mixtures, and by Professors Reinold and Rücker's communication on the Effect of an Electric Current on a Soap Film, and by Mr. Glazebrook's paper on the Optical Effect of Moisture on the Surface of Glass; while discussions of unsettled questions of importance have been introduced, among which may be mentioned that on Dusty Air by Dr. Lodge, and those on Hall's Phenomenon by Mr. Bidwell, Professor S. P. Thompson, and Mr. H. Tomlinson. It will, however, be a matter of regret to Members of the Society that some of these communications had been previously made elsewhere, and consequently Members will not be able to receive a Report of them in our 'Proceedings.' The Council trust that it may become more and more the custom for our Members to communicate their Physical work in the first instance to this Society, so that our 'Proceedings' may become a fairly complete record of the original work done in England in the Department of Physics.

The Society held a Meeting last summer in Birmingham, which gave those Members who attended an opportunity of visiting some of the most interesting Manufactories and Institutions of that town; and the Council desire to express their thanks to the Members residing there for the efficiency of the arrangements which were made.

The following circular, which has been issued to Members of the Society, explains the action which the Council have taken with respect to the International Inventions Exhibition :—

"Physical Laboratory,  
"South Kensington,  
"January 9, 1885.

"DEAR SIR,—The Members of this Society are doubtless aware that in the International Exhibition of Inventions to be held at South Kensington in the course of this year, a prominent position



will be assigned to Collections of Scientific Apparatus. It has appeared to the Council of this Society very desirable that the Society should avail itself of the opportunity thus afforded of exhibiting in a collected form any apparatus, diagrams, and appliances which relate to communications made to the Society, so as to put in evidence the work done by the Society since its foundation. The Council have accordingly applied for space for such an exhibition, to be held under their direction; and members are requested to send to one of the Secretaries of this Society the particulars of whatever they desire to exhibit. As the space at the disposal of the Society is necessarily limited, such particulars should be sent as early as possible, together with an approximate estimate of the space required. The exhibition, if made worthy of the Society, must involve some expense in arrangement and supervision, the disbursement of which out of the ordinary funds of the Society might entail postponement of the publication of the books which the Society has undertaken to issue; and, to avoid any such postponement, the Council invite from members subscriptions, which would of course be purely voluntary, for the purpose of defraying the additional expenditure.

“ Yours faithfully,

A. W. REINOLD, } *Hon. Secs.*  
WALTER BAILY, }

The Council are confident that Members will cordially assist them in their endeavours to make this Exhibition of the work of the Society as complete and satisfactory as possible. The space allotted to the Society is 36 feet long by 3 feet deep.

The Library consists of 660 bound volumes; 154 unbound and 300 separate pamphlets. During the past Session 100 volumes have been bound, and about 30 are ready for binding. The Library has been enriched since the last Report by many valuable gifts, amongst which may be mentioned:—‘The Memoirs of Coulomb,’ presented by the Physical Society of France; ‘Ronald’s Catalogue,’ presented by the Society of Telegraph Engineers; ‘The Observatory,’ by the Editor; Proceedings of the Cambridge Philosophical Society, by the Society; ‘Proceedings’ and ‘Transactions’ of the Royal Society of London, by one of our Members; Proceedings of the Royal Society of Edinburgh, also by a Member.

Early in the current year the first volume of Joule’s complete works was issued to the Members; and the Society may justly congratulate itself as having been the means of bringing out a work of such historical importance. The second volume will contain the researches of Dr. Joule in conjunction with other scientific men. The first instalment of the copy has been received from Dr. Joule,

and is now in the hands of the printer; and it is hoped that the volume will be issued during the present year.

A portion of the translation of Volta has been put in type; this must for the present be in abeyance until the Society meet with a person competent to undertake the editing of that already done and the translation of the rest.

It may here be observed that all the funds which the Society can dispose of for its reprints will be absorbed in the production of the second volume of Joule. Considering how large a number of Physicists have received the first volume as Members of the Society, the sale to the Public is not unsatisfactory; and it is confidently hoped that this sale will continue, and even increase when the work is complete. The Council would urge upon Members the importance of furthering this sale in any way they can, as on the returns thus obtained must depend the extent to which the Society can venture in this direction.

The Council regret to announce the deaths of five Members—Mr. H. R. Droop, Mr. W. R. Browne, Mr. J. F. Iselin, and Mr. R. Angus Smith.

HENRY RICHMOND DROOP, who, on his father's side, was of a North German family, was at school at Marlborough College. Thence he proceeded to Trinity, Cambridge. He took his Bachelor's degree in 1854 as third Wrangler, Mr. Routh and the late Professor Maxwell being senior and second. In due course he was elected Fellow of Trinity, and appointed a mathematical lecturer. He voluntarily resigned his Fellowship from an honourable scruple at its retention when his private means enabled him to dispense with the emolument as a means of support. His lectureship he gave up that he might study law. He became an accomplished and scientific conveyancer, and attained as much practice as he cared for. But his favourite studies were the antiquities of Ecclesiastical Post-Reformation Law, and the theory of Proportional Representation. On the former he was much consulted, both professionally and also as a friend, by barristers engaged on the anti-ritualistic side. He had made himself a thorough master of all the intricate learning of the subject. He took even a deeper interest in the defence of the parliamentary rights of minorities. On this and on ecclesiastical topics he published several thoughtful and subtle papers. He became a Member of this Society in 1879; and in the course of the long and distressing illness from which he died, he communicated to the

Society the interesting paper on Colour Blindness, which is published in the fifth volume of our 'Proceedings.' He died on the 21st of March 1884, at the age of 51.

WALTER RALEIGH BROWNE, born in 1842, was the third son of the late Rev. T. Murray Browne, Vicar of Almondsbury, and Honorary Canon of Gloucester Cathedral. He entered at Trinity College, Cambridge, in 1861, and obtained a foundation Scholarship in 1863. He took his degree in 1865, being 19th Wrangler and bracketed 10th Classic. While at Cambridge he obtained the Wrangham and Leigh Gold Medal and Prize, and in two successive years the Dealty and College Prizes for Greek Testament.

Mr. Browne was elected an Associate of the Institution of Civil Engineers in 1868, and became a Member in 1879. For a paper on "The Strength of Lock Gates," read before the Institution in 1871, a Telford Premium was awarded to him, and in 1876 his paper "On Railway Rolling-Stock," being placed first in order of merit among those read during the Session, gained a Telford Medal and Premium.

Having completed his apprenticeship as an Engineer, he became in 1874 Managing Director of the Bridgewater Engineering Company; and when, two years later, depression in trade caused these works to be closed, he was appointed Secretary to the Institution of Mechanical Engineers. This appointment he held for six years, and to the energy and ability with which he discharged his duties the Institution was largely indebted for the progress which it made during that period. He resigned the Secretaryship in 1884, and entered upon the profession of a Consulting Engineer under very favourable circumstances and with every prospect of success. In August last he went with his wife to Canada to attend the meeting of the British Association. Shortly after his arrival at Montreal he was seized with typhoid fever, and inflammation of the lungs supervening after a few days, his case became hopeless, and he died on September 4, at the early age of 42 years.

In addition to the professional interest which Mr. Browne took in matters relating to Engineering, as evidenced by his important communications to the Institutions of Civil and Mechanical Engineers, the Iron and Steel Institute, and the technical journals, he devoted considerable attention to other branches of science. He joined the Physical Society in 1880; and his papers on "Action at a Distance," "Central Forces and the Conservation of Energy,"

“The Reality of Force,” and “The Movements of Glaciers,” with the interesting discussions by which they were followed, will be fresh in the memories of many of our Members. He was a Fellow or Member of the Geological, Royal Geographical, Philological, Psychological Research, Aristotelian, and the Christian Evidence Societies. In all these he took an active interest, and to all, as also to the Royal Society, the Society of Arts, and the Church Congress, he contributed valuable papers. Many articles, signed and unsigned, which have appeared in the ‘Engineer,’ ‘Nature,’ ‘Philosophical Magazine,’ ‘Electrician,’ ‘Athenæum,’ ‘Builder,’ and ‘Church Quarterly Review,’ are from the pen of Mr. Browne. He was the author of two text-books on Mechanics; and he published admirable translations of Clausius’ ‘Mechanical Theory of Heat,’ and Schwachhofer’s ‘Fuel and Water.’

Mr. Browne was well known as a philanthropist, especially for the interest which he took in the promotion of emigration. He was also an active member of the Central Committee of the Discharged Prisoners’ Aid Society.

To those who were personally acquainted with him Mr. Browne was known as a man of kindly and genial disposition, with a wide knowledge extending over a great variety of subjects, and as one whose advice and assistance were always at the service of those requiring them, no matter at what inconvenience to himself. The bare record here given shows how full of work and usefulness was the life which has been cut short.

ROBERT HENRY SABINE was born at Dorchester in 1837. He was originally intended for the legal profession; and was for some time employed in the office of his father, who was a solicitor. But having a distaste for law and a marked inclination for scientific pursuits, he obtained an introduction to the late Sir William Siemens, who in 1858 engaged him as an assistant electrician. After two or three years, in the course of which he took part in some important experimental work, Mr. Sabine was transferred to the establishment of Messrs. Siemens and Halske at Berlin, where he was engaged principally on work in connection with submarine cables. He remained in the employment of this firm until 1867, when he started on his own account as a consulting electrical engineer. Shortly afterwards he undertook the management of some works belonging to Sir Charles Wheatstone. These subsequently developed into the British Telegraph Company, of which Mr. Sabine



was for some years Managing Director. He afterwards resumed the business of an electrical engineer, which he continued to carry on until his death.

Mr. Sabine was the author and joint-author of several important books on electrical subjects. Perhaps the most valuable and best known of these is the collection of 'Electrical Tables and Formulæ,' which he published in conjunction with Mr. Latimer Clark. His work was mostly of a practical nature; but the 'Proceedings' of the Royal Society and the 'Philosophical Magazine' contain papers by him upon purely physical subjects, those relating to the behaviour of selenium under the action of light being especially interesting.

As son-in-law of the late Sir Charles Wheatstone, Mr. Sabine was able to give the Council of the Physical Society material assistance in the preparation of Wheatstone's Scientific Papers for republication. He was one of the original Members of this Society.

He died on October 24, 1885, at the age of 47, after several months' severe illness.

J. F. ISELIN was born in Cadogan Place, London, on August 20, 1832. Two years of his boyhood were passed in Switzerland. At the age of thirteen he became a pupil in the Grammar School, Plymouth. Thence he went to Corpus Christi College, Cambridge, where he graduated in Honours in 1855, being 17th Wrangler. After four years' service as Mathematical Master in Stockwell Grammar School, he received the appointment of Inspector of Schools under the Science and Art Department; and he acted also as Assistant Examiner in Pure Mathematics in the years 1870, 1872, and 1873. It is understood that his reports showed extreme care and conscientiousness, and a great grasp of the questions which presented themselves to him. His valuable services were enlisted in the organization in London and the provinces of exhibitions of an educational character. He became a Member of this Society in 1878.

In March 1880 he was appointed Assistant Director for Science. He died, after some months' illness, on the night of November 1, 1884.

While the absorbing nature of Mr. Iselin's official duties prevented him from contributing to the common store of scientific knowledge, the very performance of those duties, as he understood them to be, has had indirectly a most beneficent effect upon Science Teaching. Of a retiring and modest disposition, the circle of his friendship



was small. The few within that circle have lost by his death a single-hearted friend. The cause of Education has lost an able and most loyal and valuable servant.

ROBERT ANGUS SMITH was born near Glasgow in 1817. After passing through the High School and University of that city, he went to Giessen, and studied chemistry under Liebig. In 1842 he settled at Manchester as Consulting Chemist, and became the author of many papers on the air and water of towns. In 1863 he was appointed Inspector-General of the Alkali Works; and on the passing of the Rivers Pollutions Act he was made Inspector for England, and afterwards for Scotland. He became a Fellow of the Royal Society in 1857, and received the degree of LL.D. of Edinburgh in 1882. He was one of the original Members of this Society.

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The Treasurer made the Financial Statement given below.

The Society then proceeded to the election of Officers and other Members of Council for the ensuing year. The Council was constituted as follows:—

*President.*—Prof. F. GUTHRIE, Ph.D., F.R.S.

*Permanent Vice-Presidents.*—Dr. J. H. GLADSTONE, F.R.S.; Prof. G. C. FOSTER, F.R.S.; Prof. W. G. ADAMS, M.A., F.R.S.; Sir WILLIAM THOMSON, D.C.L., LL.D., F.R.S.; Prof. R. B. CLIFTON, M.A., F.R.S.

*Other Vice-Presidents.*—Prof. W. E. AYRTON, F.R.S.; SHELFORD BIDWELL, M.A., LL.B.; Lord RAYLEIGH, M.A., F.R.S.; Prof. W. CHANDLER ROBERTS, F.R.S.

*Secretaries.*—Prof. A. W. REINOLD, M.A., F.R.S.; WALTER BAILY, M.A.

*Treasurer.*—Dr. E. ATKINSON.

*Demonstrator.*—Prof. F. GUTHRIE, Ph.D., F.R.S.

*Other Members of Council.*—C. VERNON BOYS; CONRAD W. COOKE;

Prof. G. FORBES, M.A., F.R.S.E.; Prof. F. FULLER, M.A.; R. T. GLAZEBROOK, M.A., F.R.S.; J. HOPKINSON, M.A., D.Sc., F.R.S.; Prof. H. MCLEOD, F.R.S.; Prof. J. PERRY, M.E.; Prof. J. H. POYNTING, M.A.; Prof. S. P. THOMPSON, D.Sc.

Votes of thanks were passed to the Lords of the Committee of Council on Education; to the PRESIDENT and other OFFICERS of the Society; and to the AUDITORS.



## PROPERTY ACCOUNT OF THE PHYSICAL SOCIETY.

ASSETS.		£	s.	d.
Balance in Bank .....		73	11	7
" due by Treasurer .....		1	1	7
Estimated Subscriptions due .....		36	0	0
£400 Furness 4 per cent. Debenture Stock .....		412	0	0
£460 Midland 5 per cent. Preference Stock .....		565	0	0
£200 Metropolitan Board of Works Stock .....		210	0	0
£214 Lancaster Corporation Stock .....		214	0	0
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		£	s.	d.
Balance .....		1511	13	2
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		£	s.	d.
LIABILITIES.				
Balance .....		1511	13	2
		<hr/>		
		£	s.	d.
		1511	13	2
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We have examined the above Account, and also the Securities at the Bank, and find the same to be correct.

E. R. FESTING,  
—C. RICHARDSON, } *Auditors.*

London, February 1st, 1885.







